



# THE CHROME TANNING PROCESS

*Its Theory, Practical Application and Chemical Control.*

BY

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WITH A

## FOREWORD

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## General Preface.

FOR a number of years the British Leather Manufacturers' Research Association has been carrying out research in the fundamental scientific principles underlying the processes of leather manufacture. During this period, much new knowledge has been accumulated in this and other countries, and it is felt that the time has come to inaugurate some scheme whereby the results of scientific work should be more generally accessible to students of leather science and to those actually engaged in supervising manufacturing processes.

There are already available a few good books on leather science. The late Professor H. R. Procter's text book on "*The Principles of Leather Manufacture*" has achieved classic fame, and J. A. Wilson's "*Chemistry of Leather Manufacture*," a newer work written from a rather more modern standpoint, presents an admirable survey of the main fields of leather science. Other valuable books on the technology of leather manufacture are also available.

Text books of a general nature, however good, have one disadvantage. Certain sections may be too condensed for special purposes and, moreover, may quickly become out of date. The re-issue of an entire volume is an expensive matter and, therefore, it has been felt that the issue of a series of moderately priced books, each dealing with a particular phase of leather science and written by a specialist in the subject, would be of great value.

The publication of such a series is now contemplated, by which it is hoped to cover the more important fields of leather trade science.

D. JORDAN LLOYD.

# Foreword,

BY

**Prof. D. McCandlish, M.Sc.**

*(Leather Industries Dept., The University, Leeds).*

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**H**ALF a century has elapsed since chrome tanning was established successfully as a commercial process of leather manufacture. Although Professor Knapp had described earlier the preparation and application of a one-bath chrome liquor, he had failed to appreciate its possibilities. It was not until 1884 that Augustus Schultz invented the two-bath tanning process which marked the beginning of what proved to be a revolutionary change in light leather manufacture. It seems very appropriate that in what is practically the Jubilee year of the Schultz discovery the present position of the science and practice of chrome tanning should be surveyed. The literature of the subject is so widely scattered that the average tanner and chemist must experience difficulty in gaining access to many important papers which are of real interest. For this reason alone, members of the leather trade will welcome the present publication which summarises in a very comprehensive manner the most important scientific and practical developments in chrome tanning since its early days. Embracing, as it does, the whole field of chrome leather manufacture, the practical tanner will find much useful information pertaining to processes and materials, whilst the leather trades' chemist will be equally interested in the exposition of the various theories of tanning. Some idea of the extent of the survey may be gained from the fact that over one hundred and twenty original papers have been consulted and their more important features summarised by the author. Dr. E. W. Merry is deserving of hearty commendation for the excellent manner in which he has produced an easily readable account of an involved subject, and students have special reason to be grateful to him for having made accessible such a large amount of necessary information in book form.

D. McCANDLISH.

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January, 1936.*

## Preface.

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**D**URING the course of an enquiry by the British Leather Manufacturers' Research Association into the present position of our knowledge of chrome tanning, a study was made of the large amount of research work which had appeared in various British, American and Continental Journals and in such well known publications as Wilson's "*Chemistry of Leather Manufacture*" and Stiasny's "*Gerbereichemie*," etc. It was later felt that a survey of the entire literature, including matter published in the confidential reports of the British Leather Manufacturers' Research Association to its members, should be made available in a convenient form to the public.

The present volume is, therefore, a summary and survey of present day knowledge on chrome tanning and, in presenting it, very grateful acknowledgment is made to the various sources from which information has been gathered, particularly to Prof. E. Stiasny and Verlag von Theodor Steinkopff for permitting the author to abstract so freely from "*Gerbereichemie*" (Chromgerbung).

It is also desired to record great appreciation of the permission granted by the British Leather Manufacturers' Research Association to publish this information, and warmest thanks to Prof. D. McCandlish and Prof. E. Stiasny for their invaluable help and interest, to the Director of the B.L.M.R.A., Dr. Dorothy Jordan Lloyd, to Dr. M. P. Balfe, to Mr. R. Faraday Innes (who provided Chapters III and IV), and to his colleagues on the Staff of the B.L.M.R.A. for their helpful criticism.

The book deals with both the one-bath and two-bath chrome tanning processes. It will, it is hoped, be found of interest to all chrome tanners and to their technical staffs, as an attempt has been made to deal not only with chrome tanning from a practical standpoint but also with the chemistry of chromium salts in general, and the various theories of chrome tanning. The chapter dealing with the chemistry of chromium salts considers the subject not only from the Werner conception of valency but also from the standpoint of the electronic theory.

The book is divided into two parts, dealing respectively with the practical and theoretical aspects of chrome tanning.

Part I can be described briefly as the practical tanner's section. No attempt has been made to deal at any length with the operations prior to the tanning process or subsequent to the operation of neutralising chrome leather. Methods for the analysis of liquors and leather are described in this part.

Part II is divided into two, Chapters VI and VII, and deals with the chemistry of the chromium salts and the modern theories of chrome tanning. Chapter VI gives a review of the present position of the chemistry of chromium. In order to obtain a clear understanding of this special branch of chemistry, it has been necessary to include an account of the modern theories of valency. All chemists who have lacked the opportunity to keep in touch with modern scientific theories should find this section both stimulating and informative.

Chapter VII, which deals with chrome tanning from a theoretical aspect, considers three main aspects of the problem, namely, (a) the reacting materials, (b) changes which can occur to these during the tanning process, and (c) the final products of the process and their properties. Various theories of chrome tanning are discussed. Chapter VII is necessarily incomplete as it would appear that the time has not yet arrived when it is possible to speak of the one theory of chrome tanning. Rather is it suggested that, according to conditions of tanning liquor and tanning process, more than one of the theories described must be brought in to explain the mechanism of the process, and according to conditions of tanning, one or other of these theories will predominate.

E. W. M.

*London, S.E.1.*

*February, 1936.*

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## PART I.

# Chrome Tanning from the Practical Standpoint.

### CHAPTER I.

#### THE PREPARATION OF TECHNICAL CHROME TANNING LIQUORS.

**C**HROME liquors are usually prepared from chrome alum, sodium or potassium dichromates or technical by-products from oxidation processes in which chromic acid has been used as oxidising agent.

If the liquors are to be made from *chrome alum*, this is made basic, usually with sodium carbonate, and in general an addition is made of neutral salts (mainly sodium chloride). Sometimes additions are made of so-called masking substances, such as sodium formate, oxalate or sulphite, with the intention of slowing up the tanning process, a procedure which is particularly desirable in the early stages if a smooth, lightly tanned grain is desired (Stiasny, 1931). Additions of other tanning materials, such as aluminium salts, formaldehyde, synthetic tannins, are sometimes made and these exert their influence upon the properties of the chrome leather. The addition of glucose or sugar to a neutralised chrome alum liquor also has an effect, giving a much fuller and plumper leather, which dries perfectly soft without even staking or fat-liquoring and without affecting the extent or rate of tanning. The effect, however (Burton, 1923), is liable to be diminished or deleted by the subsequent neutralisation, etc., of the leather.

The preparation from *dichromate* necessitates the use of reducing agents, such as glucose or sulphur dioxide, to mention but two out of the large number which is available. Each reducing agent produces its own characteristic chrome liquor, the properties of which are shown up in the leather produced from the liquor. According to Burton (1924), chrome liquors produced by the reduction of dichromates with such substances as glucose and starch produce a fuller and plumper leather than a chrome alum liquor. Similar additions to those mentioned above for chrome alum liquors are also made to reduced dichromate liquors. Reduced dichromate liquors are more difficult to prepare than chrome alum liquors. The relative cost of the two types of liquor depends largely on the prices of the chemicals involved, *i.e.*, sodium dichromate, chrome alum, etc.

*Technical by-product liquors* are used very largely in the trade and are supplied ready for use. They save the trouble involved in making liquors and have the further advantage that

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there should be no risk that these liquors contain harmful dichromates, which is always a possibility with dichromate liquors reduced in the tannery. A point to be considered by the practical man, however, who is balancing the merits of home-made liquors against technical liquors, is that liquors made in the tannery are under more direct control as regards their composition and tanning properties than bought liquors. Furthermore, alterations in the composition of the tanning liquors are much more easily carried out with tannery-made liquors than with bought liquors. The question as to which product is most suitable is frequently one of price, when it will be found that bought liquors, made in bulk quantities generally work out cheaper than tannery-made liquors.

The following summary gives the composition and characteristics of some well-known trade liquors. The particulars of the various British chrome tanning preparations were kindly supplied by the producers themselves whilst those relating to other products are taken from such sources as the *Handbuch für die gesamte Gerberei und Lederindustrie* by Wagner and Paessler and *Die Gerbstoffe und Gerbmittel* by Gnamm.

*Chrome Tanning Products* (Imperial Chemical Industries, Ltd.). The following are the products supplied by I.C.I. Ltd.

		basicity.	neutral salts.
Ammonia Chrome Alum Crystals	15.9	0	13.8 [(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ]
Chrome Sulphate Liquor REX	15.0	38.9	10 (Na <sub>2</sub> SO <sub>4</sub> )
Chrome Sulphate Liquor No. 8	15.0	32.7	12 (Na <sub>2</sub> SO <sub>4</sub> )
Chrome Sulphate Liquor XL	15.0	28.5	12 (Na <sub>2</sub> SO <sub>4</sub> )
Chrome Sulphate Powder ...	27.0	35.4	25 (Na <sub>2</sub> SO <sub>4</sub> )

It is claimed that the chrome sulphate liquors are very satisfactory for the tanning of all types of chrome leather by the one-bath process, the basicity range of 28.5 per cent. to 38.9 per cent. covering the usual requirements of the chrome tanner.

*Chromolene* (Gough Kidston & Co.). Chromolene is supplied in liquid form containing 15 per cent. Cr<sub>2</sub>O<sub>3</sub> and solid form containing 27 per cent. Cr<sub>2</sub>O<sub>3</sub>. The percentage basicity is 33 per cent. Chromolene is a sugar reduced liquor which it is claimed gives a fuller and softer leather than chrome liquors reduced by other means.

*Chrometan*, *Duo-chrometan* (Bowmans). Chrometan contains 11 per cent. Cr<sub>2</sub>O<sub>3</sub> by weight (15 per cent. by volume), 10.5 per cent. Na<sub>2</sub>SO<sub>4</sub>, and has a basicity of 33 per cent. Chrometan crystals are a concentrated form of this product. Chrometan does not contain oxidised or unoxidised organic bodies, which it is claimed have a harmful action on the pelt, or unreduced dichromate, which it is stated can cause uneven and excessive swelling, uneven dyeing and fat liquoring, and brittle grain. Duo-chrometan contains 11 per cent. Cr<sub>2</sub>O<sub>3</sub> (by weight) and 12 per cent. Na<sub>2</sub>SO<sub>4</sub>. Its basicity is about 50 per cent. By reason of its high percentage basicity it is a suitable material to use in the middle and later stages of tanning, and thus avoids the addition of sodium carbonate.

*Chrome Tanning Liquor* (Yorkshire Dyeware & Chemical Co., Ltd.). This liquor is a basic chrome sulphate liquor containing 11 per cent.  $\text{Cr}_2\text{O}_3$  and sodium sulphate. Its basicity is 33.3 per cent., but other basicities are supplied on request.

*Pancromes* (Pancrool, Ltd.). Pancromes are supplied in two grades, "CP," an  $\text{SO}_2$  reduced dichromate, and "GP," a sugar reduced dichromate giving a somewhat fuller leather. They contain about 27 per cent.  $\text{Cr}_2\text{O}_3$  and have a basicity of 33.3 per cent. The soluble salt present (sodium sulphate) is that formed during manufacture.

*Whites's Basic Chrometan* (John & James White, Ltd.). This is supplied in the form of liquor and crystals, being known as Chrometan Liquor and Chrometan Crystals respectively. Both are 33.3 per cent. basic. The liquor contains 12.5 per cent. to 13 per cent.  $\text{Cr}_2\text{O}_3$ , and the crystals 25 per cent. to 26 per cent.  $\text{Cr}_2\text{O}_3$  (percentages are by weight). The sodium sulphate content of the liquor is about 14 per cent. and of the crystals about 28 per cent.

*Hexoran Chrome Products (Liquor and Powder)* (The Hexoran Co., Ltd.). The liquor has a  $\text{Cr}_2\text{O}_3$  content of 15 per cent. by volume 13 per cent. by weight), and the powder 27 per cent. to 28 per cent. Both have a basicity of 33 per cent., but this can be varied to suit requirements. The products are offered for the production of all classes of leathers.

*Chrome E. A.* (Keiner & Co.). This chrome liquor has a specific gravity at  $15.5^\circ\text{C}$ . of 1.4000, contains 15 per cent.  $\text{Cr}_2\text{O}_3$ , has a basicity of 33 per cent., and a neutral salt content of 16 per cent. (as  $\text{Na}_2\text{SO}_4$ ). The percentages are g. per 100 c.c.

*Tanolin* (Martin Dennis), which contains 8 per cent.  $\text{Cr}_2\text{O}_3$ , is mainly a basic chloride liquor.

*Cromast, Cromul and Cromar* (Eitner). No details are given relating to their analytical composition. Cromast is produced by using thiosulphate as reducing agent, Cromul with sulphite of cellulose and Cromar with naphthalene sulphonic acid. In Cromul, the chromium is partly combined with organic materials and the material is stated to be suitable for upper leathers and combination tannages. Cromar is mainly an organic chrome compound and is stated to be suitable for the finest types of leather.

*Chromalin* (Eberle). The liquid extract contains 8 per cent.  $\text{Cr}_2\text{O}_3$  and the solid about 24—28 per cent. It is prepared from dichromate and sulphuric acid by reduction with crude glycerin (formic acid is a by-product of this reduction process). Chromalin G has a basicity of 43 per cent. and contains 30 per cent. of sodium sulphate.

The *Badische* extracts include the following:—

	% $\text{Cr}_2\text{O}_3$	% basicity.	% alkali sa
Chromacyl B (solid) ...	30	62	41.5
Chromalauge Z (extra) ...	20	37	10
„ SA (konz) ...	24	37	11
„ SF (konz) ...	28	37	0.7
Chromosal B (solid) ...	26—28	32—37	26—28
„ SA (salzarm) ...	32.5	37	14.5
„ SF (salzfrei) ...	33.5—37	32—37	1—3

*Chromgerbsalz* (Bayer) contains 36.5—38 per cent. of  $\text{Cr}_2\text{O}_3$ , 3 per cent. of alkali salts and has a basicity of 50 per cent.

*Koreon* (Röhm and Haas) contains 23·5—25 per cent. of  $\text{Cr}_2\text{O}_3$ , about 22 per cent. of alkali salts and has a basicity of 33 - 37 per cent.

*Chromobase* (Mailand) has a basicity of  $33\frac{1}{2}$  per cent. In the liquid extract the content of  $\text{Cr}_2\text{O}_3$  is 15 per cent. and 25 per cent. in the solid.

*Tannochrom* (Hamburg) contains 25 per cent. of  $\text{Cr}_2\text{O}_3$  and has a basicity of  $33\frac{1}{2}$  per cent.

Bought liquors are usually supplied in a concentrated form, and have been evaporated hot. In a hot solution of chromium sulphate, concentration drives some of the  $\text{SO}_4$  within the chromium complex forming sulphato-chrome complexes. On dilution and allowing to stand in the cold, this process is reversed and the  $\text{SO}_4$  groups in the anionic complexes are displaced by water molecules. Thus commercial concentrated chromium sulphate liquors and solid extracts contain both anionic and cationic chromium complexes. Out of a mixture of cationic chromium complexes containing OH and  $\text{SO}_4$  in the complexes, those complexes which contain the most  $\text{SO}_4$  are preferentially taken up by the hide, leaving behind the complexes poor in  $\text{SO}_4$  (Stiasny and co-workers, *Collegium*, 1928, 1929). There is abundant evidence of the existence of very complicated chromium sulphates containing both  $\text{SO}_4$  and OH in the complex. Their structural formula is a matter for speculation since the basic sulphates so far isolated have been prepared from non-aqueous solutions. The entrance of  $\text{SO}_4$  into the complex is quicker in the case of basic chromium sulphate solutions than in the case of the normal sulphate, and the addition of alkali to a normal solution of chromium sulphate accelerates the entrance of  $\text{SO}_4$  groups into the complex on ageing (Stiasny, 1928).

#### (a) *One-bath Liquors made from Chrome Alum.*

The alum generally used is potash chrome alum of a molecular weight which is near enough to 1000 for practical purposes. It contains 10·4 per cent. of chromium, whereas sodium or potassium dichromate contains  $3\frac{1}{3}$  times as much. If dissolved in water in the cold, it ionises into the following ions,\*  $[\text{Cr}(\text{OH}_2)_6]^{+++}$ ,  $\text{K}^+$  and  $\text{SO}_4^{--}$ . The chromium content of this solution can be determined from the specific gravity, a saturated solution of specific gravity 1·0885 at 15°C. containing 18·3 per cent. of chrome alum. According to Stiasny (*Gerbereichemie*, p. 422) a definite figure for the solubility of chrome alum cannot be given because the dissolved portion undergoes changes [olation of the basic products of hydrolysis (see below) and formation of sulphato-chrome-complexes (see above)]. To dissolve chrome alum in the cold, it is best either to use agitation or to suspend the alum crystals in a perforated container at the top of the water. The pH value of the cold saturated solution, freshly prepared, is 2·8. This solution, when freshly made, is violet, the colour being due to the complex ion  $[\text{Cr}(\text{OH}_2)_6]^{+++}$ ; on standing, it gradually becomes

\* In order to indicate the structural relations between the chromium atom and the water molecules in the chrome complex, the chemical formula for water is written throughout this report with the oxygen atoms adjacent to the chromium atom, hence water may be symbolised as either  $\text{H}_2\text{O}$  or  $\text{OH}_2$ .

green and progressively more acid as hydrolysis and secondary changes (formation of Ol compounds) occur. The hydrolysis gives rise to basic chromium sulphates and free sulphuric acid and the basic chromium sulphates undergo olation.

Chrome alum solutions prepared hot are green and contain strongly olated chromium compounds (Stiasny, 1931) and free sulphuric acid. Owing to these changes it is possible to prepare stronger solutions of chrome alum if the solution is prepared hot and then cooled than if the whole preparation proceeds at the ordinary temperature. Chrome alum solutions are not suitable in themselves for tanning. Satisfactory tanning properties can be imparted to a chrome alum solution by the addition of sodium hydroxide, sodium carbonate or similar alkalies. The effect of the addition of sodium hydroxide is to produce basic chromium sulphates, the nature of the compounds formed depending upon the amount added. These undergo further changes as previously described. Whereas it is easy to calculate the amount of sodium hydroxide to be added to give a desired basicity in the chrome liquor, it is not possible to forecast what will be the actual basicity of the chrome salts which are present or the extent to which they will olate, for this depends upon such conditions as concentration, temperature, age of liquor, etc. The following practical points relating to the making of liquors basic are of interest. Increasing additions of alkali (1) lower the acidity and the swelling properties of the liquor, (2) lessen the precipitation figure of the liquor, chromium salt, (3) increase the speed with which olation occurs and the extent of its occurrence, at the same time increasing the size of the chromium complex, (4) increase the colloidal character of the liquor, (5) lessen the precipitation figure of the liquor, (6) raise the proportion of sulphato groups which are held in the complex, (7) raise the astringency of the liquors, (8) increase the amount of chromium taken up by the pelt, other things being equal. Thus the preparation of mild liquors for commencing tanning requires the addition of less alkali than is the case with the later liquors in the process, which can be of a more astringent type.

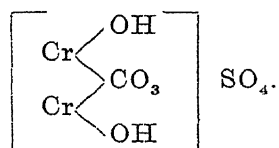
According to Lamb (1923), it is better to dissolve the chrome alum in hot water. The leather produced more closely resembles a two-bath leather as regards smoothness of grain, compactness of texture and freedom from the objectionable elasticity associated with leather made from chrome alum solutions dissolved cold.

Differences which exist between liquors made in the one case from chrome alum solutions prepared cold, and in the other case prepared hot, get less as more and more alkali is added and nearly vanish at the precipitation point (Stiasny, 1931). With moderately basic solutions, such differences are present but they are lessened by allowing the liquors to stand (ageing) and removed by heating (after making basic). According to Stiasny (1931), practical opinion about these two types of liquors is indefinite, as some tanners prefer the cold preparation, some the hot method and others find no difference between the two methods. It is evident that the practical results from these liquors must vary according to whether they are used freshly prepared or allowed to age, their basicity and the purpose for which they are prepared. For

example, for the commencement of tanning, the liquor to be preferred (Stiasny, 1931) should generally be made from cold dissolved chrome alum which contains but little olated compounds, but for completing the tannage, a strongly olated liquor is preferable, prepared from chrome alum dissolved hot.

The heating of basic chrome liquors in practice is scarcely ever met with. It should be pointed out (Stiasny, 1931) that basic chromium sulphate liquors are much more sensitive to heat treatment than are basic chromium chloride liquors.

In practice, the material used for making chrome liquors basic is usually sodium carbonate. A stock one-bath chrome alum liquor can be prepared by dissolving 10 parts of chrome alum in 80 of water and adding, with constant stirring,  $2\frac{1}{4}$ — $3\frac{1}{2}$  parts of sodium carbonate in 10 parts of water. According to Lamb (1923), 1,000 lb. of pelt to be tanned require 150 lb. of chrome alum dissolved in 50 gallons of water at about 85—95°C. The solution is rendered basic by the slow addition of 11 lb. soda ash or 40 lb. washing soda crystals in 25 gallons of hot water. The volume is finally made up to 100 gallons. The method of procedure differs considerably from that used with sodium hydroxide. For example, the addition of sodium carbonate, unlike sodium hydroxide, does not so readily produce temporary precipitates in the chrome liquor. The process of making the liquor basic can, therefore, be carried more quickly to completion (Stiasny, 1931). Furthermore, the addition of sodium carbonate to a cold chromium salt solution brings about the formation of basic complexes containing carbonato ( $\text{CO}_3$ ) groups. The sodium carbonate is not wholly used up in making the liquor basic (introducing OH groups into the chromium complex) but is partly used in the introducing of the  $\text{CO}_3$  radicle into the complex (*Gerbereichemie*, p. 425). Thus it produces liquors of a lower basicity and a different composition from those resulting from the addition of an equivalent amount of caustic soda. The type of compound produced may be represented by the formula



The addition to a cold chromium sulphate solution of 1.5 molecules of sodium carbonate for every two atoms of chromium gives a liquor with a basicity of about 36 per cent. The equivalent of sodium hydroxide would give a basicity of 50 per cent.

The complex containing  $\text{CO}_3$  is destroyed slowly by ageing and rapidly on heating, the whole of the  $\text{CO}_3$  being evolved as  $\text{CO}_2$ , and the basicity reverts to that which would have been attained by the use of an equivalent of sodium hydroxide instead of sodium carbonate. Thus "carbonato" liquors undergo the following changes on standing: they lose  $\text{CO}_2$ ; the basicity value increases for both chromium salt and liquor; olation slowly raises the acidity of the liquor. It will be seen that this is an example of a liquor which, on standing, becomes more acid (lowering of pH value) whilst the basicity increases (*Gerbereichemie*, p. 426).

According to Stiasny (1931), chromium chloride solutions form carbonato compounds more readily than do chromium sulphate solutions on the addition of sodium carbonate and, furthermore, the addition of sodium chloride to chromium chloride or sulphate liquors or of sodium sulphate to chromium sulphate liquors has no effect on the action of sodium carbonate on these liquors in forming carbonato salts.

The addition of sodium carbonate to a hot chromium salt solution does not lead to the formation of carbonato salts, but gives liquors which resemble liquors made basic with sodium hydroxide and then heated (Stiasny, 1931). Thus chrome liquors prepared by reducing dichromate with organic reducing agents (glucose, etc.) in which there is a large evolution of  $\text{CO}_2$  during the reducing process, are free from carbonato salts if the reduction is carried out hot.

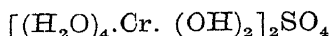
The carbonato salts in a tanning liquor are affected but little during the tanning process so that the liquor containing these salts will have different tanning properties from a liquor made basic with sodium hydroxide (Stiasny, 1931).

Chrome alum solutions may also be rendered basic by the use of sodium thiosulphate. According to Lamb, such a liquor may be made up as follows: for 750 to 800 lb. of pelt, 100 lb. of chrome alum is dissolved in 25 gallons of water by boiling. When solution is complete and with the solution boiling, 24 lb. of sodium thiosulphate dissolved in 5 gallons of water is added slowly. The mixture is boiled for 20–30 minutes and finally made up to 50 gallons. Eitner (*Handbuch für die gesamte Gerberei und Leder-Industrie*, p. 206) recommends the slow addition of a solution of 5 kg. of thiosulphate in 15 l. warm water to 20 kg. of chrome alum dissolved in 80 l. warm water and allowing the solution to settle. To avoid the final boiling treatment Koehler (1929) recommends adding sufficient dichromate to use up the sulphur dioxide set free by the addition of the thiosulphate. A short heating is, however, desirable to decompose any dithionates. The action of thiosulphate in the cold upon chrome alum leads to the formation of olated basic sulphito-sulphato-chrome complexes. pH values as high as 4.5 can be attained without the separation of insoluble basic chromium salts (Stiasny and Prakke, 1933).

Besides using chrome alum and sodium carbonate in the preparation of chrome liquors, an addition is also made of neutral salts, generally sodium chloride. This has for its purpose the checking of undesirable swelling of the pelt, particularly of the grain. It also gives a light pickling treatment and lessens the astringency of the chrome liquors (Stiasny, 1931). As shown by Burton and Glover (1922) it slows up the tannage so that it takes longer for the pelt being tanned to pass the boiling test and also lessens the amount of chromium taken up by the pelt. Wilson and Kern (1917) found that the addition of neutral salts raised the precipitation figure. This increase was greater with additions of sulphates than of chlorides and the effect was greater the more basic the chrome liquors.

The practical man is familiar with the action of additions of sodium chloride, in bringing about a smooth soft grain and the production of empty flat leather, caused by the addition of too much salt (Stiasny, 1931).

Different in type altogether is the effect of the addition of sodium sulphate to basic chromium chloride liquors, for these then take on the properties of basic sulphate liquors (Stiasny, 1931). The precipitation figure drops considerably and if the basicity of the chromium chloride liquor is sufficiently great, the addition of sodium sulphate cause precipitate formation. Care must, therefore, be taken in practice when adding sodium sulphate, chrome alum or basic chromium sulphate liquors to basic chromium chloride liquors. It must be remembered that the basic chromium sulphate,



is insoluble in water whilst the corresponding basic chromium chloride,  $[(\text{H}_2\text{O})_4.\text{Cr.}(\text{OH})_2]\text{Cl}$ , is soluble.

In practice, the addition of sodium sulphate to chromium chloride liquors gives a fuller leather (Stiasny, 1931).

(b) *One-bath Liquors made from Dichromates.*

Dichromates are reduced in the presence generally of sulphuric acid, or sometimes hydrochloric acid, by means of a suitable reducing agent. Whilst in two-bath chrome tanning the reducing agent must be effective in dilute solution and rapid in action at room temperature (usually thiosulphate is used for this purpose), the choice of the reducing agent in the preparation of one-bath liquors is much greater. Fundamentally, any material which reduces chromic acid in hot, fairly concentrated solutions may be used (Stiasny, 1931). For example, the following inorganic materials: sulphur dioxide, sodium sulphite, sodium bisulphite, sodium thiosulphate, sulphides, hydrogen peroxide, etc., and the following organic substances: glucose, cane sugar, molasses, glycerin, cellulose extracts, spent vegetable tanning materials, oxalic acid, etc., will bring this about.

Sulphuric acid is the acid most used in preparing technical tanning liquors. Organic acids have been stated to be less suitable (Stiasny, 1931) and they are not used technically to any great extent. Mixtures of acids such as sulphuric and an organic acid could be, but do not appear to be used. In a few cases, the reducing agent is also an acid and the addition of a further acid would not be necessary, for example, sulphurous acid, sodium bisulphite and oxalic acid.

Where acid has to be used in addition to reducing agent, then the amount used is governed by the desired basicity of the chrome liquor. This basicity cannot be greater than a certain amount, depending on the nature of the reduction, as a certain amount of acid is necessary in order that the reduction process may be brought to completion. The amount of acid to be used can only be calculated in those cases where the reducing agent neither consumes nor produces acid by its oxidation or where the chemistry of the production or consumption of acid is clearly defined stoichiometrically. The following are examples where no consumption or production of acid occurs; hydrogen peroxide, sodium bisulphite (if excess be avoided), glucose (provided conditions of concentration and temperature are maintained so that oxidation to  $\text{CO}_2$  and water occurs). In such cases (Stiasny, *Gerbereichemie*,

p. 432) the equation  $n = 133.8 - a$  gives the amount ( $n$ ) of sulphuric acid per 100 parts of dichromate, which is necessary to obtain the desired degree of basicity ( $a$ ).

In the preparation of one-bath liquors from dichromates, care must be taken that the reduction is complete. This can be easily tested as follows: a few drops of the liquor are placed in a test tube, diluted with about 5 c.c. of water, ammonia is then added and the mixture boiled and filtered. If reduction is complete the filtrate should be colourless. If the filtrate is yellow, then unreduced chromate is present, provided the reducing agent (as is the case with some organic by-products) does not of itself cause the yellow colour. In order to find out whether the chrome liquor in course of preparation requires more reducing agent or more acid or both, to complete the process, it is usual to take samples of the liquor, to add more reducing agent to one, more acid to another and both acid and reducing agent to a third test. The three samples are then tested after a short time for the presence of unreduced dichromate. A more convenient method for testing for unreduced dichromate is that described by Treadwell (*Qualitative Analysis*, 14th Edition, p. 161; see also Stiasny and Papayannis, 1934). 2 g. diphenyl-carbazide are dissolved in 10 c.c. glacial acetic acid and alcohol is added to bring the volume to 200 c.c. A few drops of this reagent are added to a small amount of the diluted chrome liquor. The formation of a violet coloration indicates the presence of unreduced dichromate.

It is not generally recognised (Stiasny, 1931) that it is not the same thing to carry out the reduction process so as to give a final liquor of a definite desired basicity as to adjust a liquor of an incorrect basicity by adding acid or alkali. A liquor which has been corrected by the addition of sodium carbonate olates on standing, becomes acid and gradually increases its precipitation figure. If corrected with an acid ( $H_2SO_4$ ), then the opposite occurs, on standing the liquor becomes less olated, less acid and suffers a reduction in its precipitation figure. Changes such as these receive at the present time little consideration, but according to Stiasny (1931, p. 432) they explain very many irregularities which are met with in the tannery.

#### (a) Glucose Liquors.

The use of glucose in the preparation of one-bath chrome liquors was suggested as long ago as 1897 by Procter, who recommended the following quantities: 3 parts by weight of dichromate, 6 parts by weight of concentrated hydrochloric acid or 3 parts of B.O.V. (concentrated commercial sulphuric acid). When reduction is complete, make up to 100 parts. The reduction is brought about by the continuous addition of sugar, which keeps the whole mixture at the boil. Procter preferred cane sugar to glucose since he considered the latter was at that time often contaminated with materials, the oxidation of which reduced the tanning properties of the chrome liquor. Another method which is attributed to Procter (*Handbuch für die gesamte Gerberei und Leder-industrie*, p. 206) is the following: 6 kg. dichromate are dissolved in 15 l. of hot water (80–90°), 5 kg. of sulphuric acid (66° Bé) are slowly added and the mixture is thereby brought to a boil, 4 kg. glucose

dissolved in 10 l. of water are slowly added. On the laboratory scale, about 15 per cent. of sugar (percentage on the weight of dichromate), that is the theoretically calculated amount, is nearly enough to give complete reduction, but on a works' scale, larger amounts must be used, since the practical conditions gradually become less and less suitable for the oxidation of the sugar to  $\text{CO}_2$  and water (Stiasny, 1931). The formation of intermediate products of the oxidation of the sugar has also to be considered. These can lower the basicity of the liquor (acidic substances), and can also exert a masking action in that they enter the chromium complex and shield this against the precipitating action of alkalis and at the same time reduce the astringency of the chrome liquor. In order to reduce the masking action to a minimum, the use of an excess of sugar must be avoided. The more complete the oxidation, the less is the formation of intermediate oxidation products. A lowering of the temperature at which reduction is allowed to take place, for example, lowers the basicity of the final liquor.

Of the liquors prepared by the tanner himself in the works from dichromate, glucose reduced liquors are the most widely used. The methods of preparation differ considerably and result in tanning liquors which have particular properties according to the method used. Variations occur in practice in the choice of acid (sulphuric or hydrochloric acid), the proportion of glucose to dichromate, the proportion of acid to dichromate, and also in the order of addition of the various materials used in the reduction process. In some cases, excess of glucose is carefully avoided by completing the final stages of reduction by the addition of another reducing agent, such as sodium bisulphite. In other cases, an excess of glucose is deliberately added. With reference to the order of addition, the glucose can be added slowly to the hot mixture of dichromate and acid or the acid slowly to a hot mixture of dichromate and sugar, or finally, the dichromate can be added to a mixture of sugar and acid of medium strength. The experiments of Stiasny and Ziegler (1931) attempt to throw some light on the result of such variations in procedure. These workers found that the pH values of the resulting liquors varied, according to the amount of sulphuric acid used, between 2.85 and 3.4. After three weeks standing, the complex chromium ion was kationic in every case. If  $n$  = the amount of sulphuric acid added to 100 parts of dichromate and  $a$  = the percentage basicity of the reduced liquor, then  $a - [133.3 - n]$  is a measure of the organic acids produced by the oxidation of glucose. In the case of hydrochloric acid (instead of sulphuric) the formula is  $a - 2.48 [133.3 - n]$  where  $n$  is the amount of 30 per cent. hydrochloric acid per 100 parts of dichromate (Stiasny, *Gerberei-chemie*, p. 436). In the preparation in which the glucose solution was added to a mixture of dichromate and sulphuric acid, volatile acids were produced but oxalic acid was absent from the final liquor. The use of an excess of glucose or too little sulphuric acid increased the production of volatile acids. Where the procedure was to add the acid to the dichromate-glucose mixture, the liquors contained larger amounts of volatile acids than where the procedure was to add the glucose to the acid and dichromate mixture. Oxalic acid was present when the acid was added to the dichromate-glucose mixture or the dichromate to the glucose-acid mixture.

With glucose containing dextrin, larger amounts of reducing agent are required than when the glucose is free from dextrin. Acid formation and masking are not increased by the use of glucose containing dextrin. The precipitation figure is affected by the amount of acid used and the amount of masking which occurs.

The temperature of the reduction mixture also affects the final basicity, as shown by Barber and Barker (1917). The higher the temperature, the greater the expulsion of volatile acid oxidation products and the greater the percentage basicity of the resulting liquor.

Thus it is evident that in the production of glucose reduced liquors, the working conditions must be strictly adhered to if chrome liquors are required of constant properties which will be regular in their behaviour in the tan-yard.

Glucose liquors are recommended for enamelled leathers by Hanglin (1933).

(β) Liquors prepared by using organic by-products as reducing agents.

Eitner (1901) suggested the use of cellulose extracts and used these in the preparation of "Cromul." The concentrated cellulose extract is added to a hot acid dichromate solution until reduction is complete. 100 parts of dichromate, 45.7 parts of cellulose extract (33 per cent. organic dry residue) and 91.2 parts of sulphuric acid gave a liquor of basicity 30.7 per cent.

The use of spent tanning materials was suggested by Stiasny in 1902 and recommended in his lectures given in the Leather Industries' Department at Leeds University. J. R. Blockey independently used this method about 1920. The Blockey (Wm. Walker & Sons, Ltd., of Bolton) patent specification covers the use of spent tan, waste leathers, tan-pit sludge, bloom, ellagic acid, phlobaphenes, sawdust, wood shavings, etc. Air-dried spent tan is added to a hot mixture of dichromate and mineral acid until reduction is complete. Reduction is slow and the temperature should be maintained by the use of steam. In the last stages of the reduction the liquor is filtered through a bed of spent tan and small amounts of unoxidised tan pass into the liquor. This, in the tanning process, imparts a yellowish tinge to the grain of the material being tanned, which can be utilised if it is desired later to dye the tanned material. The reduction process can be assisted towards the end by the addition of other reducing agents, such as bisulphite.

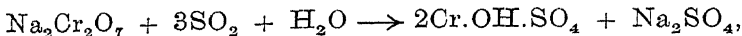
Other reducing materials which have found practical application are glycerin, wood sawdust and potato starch.

Glycerin was used by the Eberle firm in the production of "Chromalin." Its action is very violent but uniform. For 100 lb. of dichromate and 100 lb. of sulphuric acid, 33 lb. of glycerin are necessary. The final liquor contains as by-products, glyceric acid, tartronic acid and formaldehyde, and is a similar tanning liquor to a glucose-reduced liquor.

(γ) Sulphur dioxide liquors.

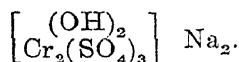
The passing of sulphur dioxide into a dichromate solution produces a chromium sulphate liquor which, after boiling to remove excess of sulphur dioxide, has a basicity of 33.3 per cent. The

preparation is cheap and simple and the properties of the chrome liquor can be altered as desired by the addition of alkali, neutral salts or masking substances (Stiasny, 1931). The sulphur dioxide can be obtained in gas cylinders or prepared by burning sulphur or pyrites in a suitable oven. The change can be represented as follows:—



and the final liquor, which is a deep bluish green, always has the above basicity. The use of a slight excess (about 5 per cent.) of sulphur dioxide is advisable. 100 kg. of dichromate requires 70 kg. of  $\text{SO}_2$  (theoretical = 65.3 kg.). The excess of  $\text{SO}_2$  should be boiled off. The actual stages by which the above end-products are reached is not so simple as suggested in the equation. According to Stiasny (1931, p. 437-9), in dilute dichromate solutions the sulphur dioxide is oxidised in the cold to dithionic acid ( $\text{H}_2\text{S}_2\text{O}_6$ ), which later oxidises to sulphuric acid. Sulphuric acid is also formed in concentrated dichromate solutions, especially at higher temperatures. The formation of chromium dithionate has also been observed and with differing dichromate concentrations and temperatures, so the composition and electrical nature of the chromium complex varies, giving, for example, chromium dithionate (kationic chromium complex) and an anionic chromium complex containing  $\text{SO}_4$ .

The more concentrated the solutions used, the more this favours the formation of anionic basic chromium complexes containing  $\text{SO}_4$  in the complex. In the extreme case, if the liquors are evaporated to a syrupy consistency, then only anionic chromium complexes are present with all the  $\text{SO}_4$  within the complex (Stiasny, 1931). These complexes are completely masked against the action of barium chloride in the presence of hydrochloric acid and also 0.5*N* alkali. They may be represented by the formula



These facts emphasise the importance of the recommendations of Procter that standard conditions should be maintained during the reduction process, etc.

According to Lamb (1923, p. 162), the leather produced by the use of a sulphur dioxide reduced liquor is lacking in fullness and plumpness compared with that obtained with a liquor prepared with an organic reducing agent.

#### (8) Sodium sulphite liquors.

Dichromates can be reduced by sodium sulphite with or without the addition of acid. With acid,  $\text{Cr}_2(\text{SO}_4)_3$  is formed. Without acid, the reduction is complete but, according to the concentrations used, may give rise to a certain amount of anionic basic chrome complexes containing  $\text{SO}_3$  and  $\text{SO}_4$ .

Reduction by sodium sulphite has been patented and the process is described as follows: 525 kg. of sodium sulphite are added slowly during 60 minutes to a mixture of 300 kg. of sodium dichromate in 1500 litres of water and 500 kg. of 50° Bé sulphuric

acid. Agitation is continued for another hour at 75—80°C. The chrome salt formed has to be made basic by the addition of more sulphite (60—100 kg.). Hydrochloric acid can be used instead of sulphuric acid.

(e) Sodium bisulphite liquors.

“Bisulphite” liquors, *i.e.* dichromate reduced by sodium bisulphite, are liable to undergo a process of jelly formation on standing which limits their use for practical purposes unless the jelly formation is prevented. This can be achieved by preparing the “bisulphite” liquor in another chrome liquor, for example, in a basic chrome alum liquor (Stiasny, 1931). The dichromate is dissolved in this liquor and reduced in the cold with sodium bisulphite. The preparation gives mixed chrome liquors, with valuable tanning properties, which can contain 70—80 per cent. of the chromium in the form of a “bisulphite” liquor with neither jelly nor precipitate formation on standing.

According to Stiasny (1931, p. 439 - 440), tanning experiments show that the greater the proportion of “bisulphite” liquor present in the mixed liquor, the greater is the amount of chromium taken up in tanning and, furthermore, unpickled pelts take up considerably more chromium than pickled.

“Bisulphite” liquors are recommended for chrome black and coloured upper leathers by Hanglin (1933).

(η) Thiosulphate (Hypo) liquors.

Dichromates can be reduced by acid and thiosulphate in such a way that clear liquors are formed and there is no separation of sulphur (Stiasny, 1931). The sulphur may be present as a colloidal solution since it separates if the liquor is allowed to age and is deposited in the leather during tanning, thereby bringing about a filling action. The preparation of thiosulphate liquors is best carried out by using strongly concentrated hot solutions (Stiasny, 1931), adding the concentrated thiosulphate solution slowly with efficient stirring and avoiding an excess of thiosulphate throughout. When the liquor becomes olive green and a test shows that a slight amount of unreduced chromate is still present, the addition of thiosulphate is stopped and the liquor allowed to stand overnight. If the reduction is still incomplete, it is completed by the addition of bisulphite. The amount of thiosulphate depends upon such conditions as concentration, temperature and speed of addition. Many reactions are proceeding during the reduction and the thiosulphate is oxidised to sulphate, sulphuric acid, sulphur, tetrathionate and pentathionate. The following practical details are given by Stiasny (*Gerbereichemie*, p. 441). 100 kg. of sodium dichromate are dissolved in 100 l. of water warmed to 50°C. and then brought to the boil by the rapid addition with agitation of 90 kg. of concentrated sulphuric acid. A solution of 120 kg. of thiosulphate in 120 l. of water is then added in a thin stream with vigorous stirring until the reduction is nearly complete. Then the procedure is as described above.

Another formula which gives a satisfactory liquor (according to Crockett, 1921), is to use 100 lb. of sodium dichromate, 87.7 lb. of pure sulphuric acid and 110 lb. of sodium thiosulphate; and yet another, 100 kg. dichromate in 500 l. of water, 90 kg. of sulphuric

acid at 66° Bé and 150 kg. of thiosulphate in 200 l. of water. The high price of sodium thiosulphate and the separation of sodium sulphate crystals in cold weather are the drawbacks to this type of liquor.

With all reduction processes involving the reduction of chromic acid by organic materials, consideration must be given to the fact that the choice and maintenance of the reduction conditions govern the production of greater or smaller amounts of oxidised intermediate substances, some of which volatilise to some extent during the preparation process and affect the tanning properties of the final liquor. From a practical standpoint, those chrome liquors are to be preferred which are free from fluctuating amounts of masking substances and to which the practical tanner can make suitable, controlled additions, thereby imparting to the chrome liquor the tanning properties desired.

Unreduced chromates should not be left in the so-called reduced liquors since in such a case the resulting chrome blues can contain appreciable amounts of chromate. Moreover, such procedure is neither economical, nor are the liquors reliable in composition. Not only is the nature of the chromium content affected, but the basicity of the chromium salt is also disturbed by variations in the chromate content. Such liquors must be considered as unsatisfactory.

Another point to be emphasised, which has been considered earlier, is the effect on a basic chrome liquor of evaporating it to produce a concentrated or even a solid extract. By this treatment, water leaves the chrome complex and is replaced by acid groups. This leads to an alteration in the constitution of the dissolved chromium compound. A medium basic, partly olated kationic chromium complex with  $\text{SO}_4$  outside the complex can give rise to a strongly olated anionic chromium complex containing  $\text{SO}_4$  within the complex with completely different properties and tanning action. The chromium and  $\text{SO}_4$  have become masked or protected against the precipitating actions of 0.5N ammonia, even on boiling, and also of those of barium chloride in the presence of hydrochloric acid. If the concentrated liquor is diluted and allowed to stand for several hours, a gradual reversal takes place of the changes brought about by concentrating but it can take days before the addition of ammonia gives an immediate precipitate and the restoration of the  $\text{SO}_4$  to its ionic condition is even slower. The presence of alkali sulphates in the chrome liquor assists the change described above, *i.e.* the formation of anionic chrome complexes containing  $\text{SO}_4$ .

The process of reduction of dichromates is accompanied by the evolution of a considerable amount of heat. Whereas on a laboratory scale the dissipation of this heat occurs sufficiently rapidly to make it easy to keep the temperature of the reaction under control, on a large scale where material is being handled in bulk, the dissipation of heat may occur comparatively slowly, since the surface of dissipation promoting heat loss is small relative to the bulk of reacting materials producing the heat, with a consequent rise of temperature to dangerous heights. The installation of large scale plant and processes should only be undertaken under the supervision of a chemical engineer. Otherwise, the

reduction operation in unskilled hands and with unsuitably designed plant can become very dangerous as the result of an uncontrolled rise in temperature of the reacting materials.

The reduction process is usually carried out in lead (soft lead for preference) lined wooden vessels, fitted with stirrers and shields. The operatives should be provided with protection against spray consisting of tiny drops of dichromate, for these attack the skin (particularly the mucous membrane) and can lead to dangerous chrome poisoning. Treatment with thiosulphate solutions, *i.e.* washing, is recommended. People who are sensitive to chromate poisoning should not be employed either in the powdering, weighing or dissolving of dichromate or in the operation known as the first bath in the two-bath chrome tanning process.

## CHAPTER II.

### SOME FACTORS IN THE ONE-BATH CHROME TANNING PROCESS.

#### (a) *Practical Procedure.*

ACCORDING to Stiasny (1931), in one-bath chrome tanning, it is generally advisable to start the process with liquors which are only slightly astringent and then continue and complete the tannage with liquors of increasing astringency. Care must be taken to avoid a heavy tannage of the grain and yet at the same time to tan the rest of the material satisfactorily. The former is the chief difficulty, as a finished chrome leather is judged very largely upon the properties of the grain and how these properties vary in different parts of the same skin. Other properties of the leather, such as feel, elasticity, thickness, etc., and the variation of these properties in different parts of the skin must not be lost sight of, but it is of special importance to devote considerable attention to the tannage of the grain. Tanning with chrome liquors is not exactly analogous to tanning with vegetable tan liquors, since the latter on dilution become less astringent, whereas one-bath chrome liquors, on dilution, do not become less astringent. Dilution facilitates hydrolysis of the chromium salt, the basicity of the chrome salt increases, leading to the formation of higher molecular complexes of increased astringency. According to Stiasny (*Gerbereichemie*, p. 447), the golden rule of tanning is: Start with liquors containing small particles and continue with particles of increasing size. Thus chrome tannage should, in general, commence with liquors of low basicity and continue with increasing basicity. This can be achieved practically by the periodic addition of solutions of sodium bicarbonate or borax during the course of the tanning, but the amount of alkali added will depend upon the amount of acid in the skins and also upon the nature of the tannage. The custom of pickling before tanning can be explained in the light of the recent work on the chemistry of chromium. Pickling not only brings the skins into a uniform condition of acidity but it also adjusts the basicity of the chrome

liquors checking olation, delaying precipitation and keeping the liquors mellow. In the early stages of chrome tanning, the pelt takes up considerable amounts of acid unless it is in a pickled condition, when it may even give up acid to the tanning liquor. In practice, pelts before tanning are nearly always pickled and the type as well as the rate of tannage is affected by the manner of pickling, *i.e.*, the acid and salt concentration not only controls the rate and amount of chromium taken up and thus the composition of the chrome tanning salt, but also the colour of the chrome leather in the blue.

According to Stiasny (*Gerbereichemie*, p. 450 - 454) the details of the actual tanning process can vary tremendously. In one process the pickled pelts are allowed to drain and then passed into a 5—10 per cent. solution of sodium chloride in a drum. After running a short time, the first few minutes of which removes a considerable amount of the pickle acid, the chrome liquor, suitably adjusted for basicity, is periodically added. The salt prevents undue swelling of the pelts. The acid in the pelt lowers the basicity of the chrome liquor and its precipitation figure is raised by the salt. These changes are all in the direction of producing a slow, gentle tannage of the grain, thereby protecting the grain against the action of the later more astringent liquors which complete the tannage. The total amount of liquor in drum tanning is about 100—150 per cent. and the chromium used is about 1.5—2.5 per cent. of the pickled pelt weight. The time of tanning is about 6—8 hours for calf, 5—6 hours for sheep and goat and 10—12 hours for ox hides. If after these times the material does not stand the boiling test, repeated additions of well-diluted sodium carbonate solution may be carefully and slowly made, avoiding local precipitation, the goods being drummed during and after each addition. The tannage is complete when the boiling test is satisfactory. Excess of sodium carbonate at any stage must be avoided and the tanning liquor must not be allowed to reach the point of precipitation, otherwise there is a risk of a loose, discoloured, pipey grain. The determination of this pre-precipitation point or precipitation figure by the method of McCandlish (1917) can act as a guide to the addition of sodium carbonate. Lack of care in the addition of the alkali in chrome tanning leads to uneven deposition on the grain of the goods with subsequent irregularities in dyeing and fat-liquoring.

In another process, the pickled goods are left in the drum, one-half to two-thirds of the spent pickle is run off and a suitable chrome liquor (of high basicity and low precipitation figure) added gradually while drumming proceeds. The protective action of the pickle on the grain, especially if the pickle is rich in acid, is greater than in the previous method, and quite astringent chrome liquors may be used, in which case it is not necessary to make any additions of sodium carbonate.

In order to bring about a better exhaustion of the chrome liquor, one-half to two-thirds of the residual liquor left after tanning a pack of goods can be used for the next pack. For example, the pickled and drained pelts are brought into a drum containing once used tan liquor, 5 per cent. of sodium chloride (on the pickled pelt weight) and water to bring the volume to 100—150 per cent.

After 1—2 hours running of the drum, most of the drum liquor is run off and then the rest of the old tan liquor, plus fresh tan liquor is run in. The tannage is completed by the usual addition of sodium carbonate.

It is generally to be recommended to complete the tannage without the addition of sodium carbonate, *i.e.*, by the use of more basic chrome liquors towards the end of the tannage and, if necessary, replacing a portion of a lesser basic liquor by an amount of a more basic liquor.

In a further modification, the pickled pelts may be left in the drum, part of the pickle run off, the used chrome liquor containing 5 per cent. of sodium chloride (on the pickled pelt weight) added. The drum is run 1—2 hours, after which most of the drum liquor is run off and replaced by fresh chrome liquor, which is gradually strengthened from time to time.

Again, the drained pickled pelts can be brought into a liquor containing 100 per cent. of water, 5 per cent. of chrome alum (or another 0 per cent. basic chrome liquor) and 5 per cent. of sodium chloride. After 30—60 minutes' drumming, the liquor can be strengthened by adding a 40—50 per cent. basic chrome liquor and then, in general, the procedure is as above.

The tannage of unpickled pelts can be started by drumming the pelts in a solution containing 100 per cent. of water, 10 per cent. of chrome alum and 5 per cent. of sodium chloride and the tannage continued by the gradual addition of a 40—50 per cent. basic chrome liquor.

The common principle of these methods is to have the tanning liquor of increasing basicity and lessening precipitation figures, that is, of increasing astringency. This is also the case where the whole of the tanning liquor is added in one lot at the beginning of the tannage. Drumming should be carefully controlled since a rise in temperature must be avoided, especially at the commencement, when the goods are still sensitive to heat. A moderate rise towards the end is not a disadvantage as it accelerates the final stages of the tanning and spends the liquor better (*Second Annual Report of the British Leather Manufacturers' Research Association*, 1922).

A special type of chrome tanning (Schorlemmer, 1922), in which pickling is avoided, time and power are saved and very little effluent is left, is that known as "dry tanning." In this, the bated or delimed pelts are not pickled, small volumes of tan liquor are used (about 30 per cent. on the pelt weight) and the tan liquor used is concentrated, containing 4—5 per cent. of chromium (1.5—2 per cent. of chromium on the pelt weight). The whole is drummed together for 30 minutes, the liquor is completely absorbed, the goods are allowed to stand for several hours and then horsed up for 2 days. The spending of the liquor is 85—95 per cent. of the chromium originally present. The strong liquor used above is very mellow since concentration decreases hydrolysis and thus decreases astringency. The chrome salt taken up by the pelt is less basic in the "dry" tanning than in weaker liquors of the same type (Berkmann, 1925). According to Wilson, the main disadvantage of this method of tanning is the difficulty of controlling concentrations accurately.

In "dry" chrome tanning, the addition of sodium chloride alters the softness and colour of the leather. It is, therefore, recommended (Stiasny, 1931) that it be added when tannage is complete. The following example illustrates this point. 100 kg. of pelt are tanned with 10 kg. of basic chromium chloride (25 per cent.  $\text{Cr}_2\text{O}_3$  and 50 per cent. basic). When tanning is complete, 10 kg. of salt are added and drumming continued for 1 hour.

In tanning with chrome salts, it is possible to vary the nature of the liquor and the conditions of tanning to give a very wide range of leathers from sole to flexible belting, such as picker bands. Furthermore, the tannage may be carried out in drums, paddles or pits. Drum tanning gives an advantage in saving space and time. For example, a tannage system taking 6—10 days in pits can be carried out in 6—10 hours in the drum.

If hides are drum tanned, the basicity of the starting liquor must be low enough to avoid case-hardening, which occurs with too basic liquors, and low enough to avoid bringing about an undue reduction in the thickness of the hides. After drumming about  $1\frac{1}{2}$ —2 hours, the basicity can safely be raised to about 28 per cent. by adding soda crystals dissolved in water. Later the basicity can be further raised in the same way to about 36 per cent. When penetration is complete (by examination of a cut) and the tannage is satisfactory (by the boiling test), the goods are horsed up for a time and then neutralised, using 2 per cent. borax or 1 per cent. of sodium bicarbonate, washed and dried out.

In the pit process, for the production of chrome sole, two or more pits in series are used and the hides are suspended in a series of liquors of different strengths. The goods are moved forward from pit to pit as in vegetable tanning, and they can also be rocked with advantage. The tannage is started in weak liquors of low basicity or even liquors to which acid has been added (to neutralise any alkali brought forward by the hides). The successive liquors increase in chromium content and in basicity, the tannage finishing with a liquor of about 36 per cent. basicity and up to 45° Bk. The weakest or first liquor in such a set is thrown away after each pack and the pit is made up fresh to become the last and strongest pit for the series, the second pit becoming the weakest, and so on. The tanned goods are horsed up and neutralised as usual, using a 0.5 per cent. solution of sodium bicarbonate or a 1 per cent. solution of borax in a pit.

The two-bath process is generally used for chrome picker bands, but if one-bath chrome liquors are employed, it is advisable to use hypo in the preparation of the liquors for reducing the dichromate and during the process for increasing basicity, as this helps in producing a more suitable leather.

For chrome belting the goods are generally completely delimed, usually with boric acid. This assists in giving regularity of tanning in chrome tanning with no undue disturbance of the basicity. With pickled goods, sodium chloride should be added to the chrome liquors to prevent undue swelling and the chrome liquors can be more basic to neutralise the acid taken in by the goods. With undelimed goods, the chrome liquors at the start generally have acid added to neutralise the lime taken in.

Thus the early liquors must be adjusted to meet the goods entering whether limed, delimed or pickled.

The one-bath chrome tanning process is slower than the two-bath process, the difference being a question of speed of penetration. An "acid" liquor penetrates quickly but gives an empty tannage. The use of too basic liquors gives a heavy tannage on the outsides with a risk of under-tannage of the centre. Hence has arisen the practical procedure of working from low to higher basic liquors to give uniform penetration.

In one-bath chrome tanning, the composition and properties of the finished leather are affected by many factors relating to the tanning process, such as (1) the state of the goods entering the chrome liquors, *i.e.*, pelt tanned in the fallen state tends to be soft and pliable; (2) the type of tanning liquor [according to Burton (1923), an  $\text{SO}_2$  reduced liquor which seems to have a tendency to produce a closer grain is better suited for leathers which are to be fat-liquored, such as boot and shoe upper leathers, whereas for leathers which are to be stuffed and where a more open texture and greater plumping are desirable, a glucose reduced liquor is more suitable]; (3) the speed of tanning which increases as the precipitation figure decreases (Burton, 1920); (4) the composition of the chromium complex; (5) the concentration of chromium; (6) the presence of neutral salts; (7) the pH value; (8) the progress of the simultaneous swelling and structural alterations of the hide (the amount of swelling produced by a chrome liquor is one of the main factors in determining the properties of the chrome leather); (9) temperature; (10) time; (11) mechanical treatment; (12) proportion of liquor to goods; and so on. The effect of some of these factors will now be considered.

#### (b) *The Effect of pH Value.*

An increasing pH value in the chrome tanning liquor causes the molecules of the chromium salt to become larger and larger. This reduces the rate of penetration of the tan into the skin and the risk of over-tannage of the grain increases. Free acid present in the tanning liquor penetrates the skin more rapidly than the basic chrome salt, thereby causing the chrome liquor to become more basic and more colloidal. This differential diffusion of acid and chrome salt does not occur to the same extent where the goods are acid (pickled). If, however, the skins contain an excess of acid, the chrome tan diffuses rapidly. The chrome liquor within the pelt is correspondingly more acid and the rate of combination of protein and chrome tan is reduced. This procedure helps considerably in preventing over-tannage of the grain. It becomes necessary, however, to neutralise some of the acid before the skins can become completely tanned, even though completely penetrated by the green chromium salt. This is achieved by the periodic additions of sodium carbonate, bicarbonate or borax during the tanning process. By suitably arranging conditions, the pH value and chromium content can be made to vary within suitable limits, each limit yielding a leather having certain characteristics. The range of possibilities is thus enormous. Some pH values for basic chromium sulphate solutions are given on p. 111, and chromium nitrate solutions on p. 107.

(c) *The Effect of Concentration.*

Dilution of a chrome liquor lessens the chromium concentration. It also displaces the hydrolysis equilibrium and thereby sets free more acid, increases the basicity of the chrome salt, increases the hydrolysis of the basic chrome salt, assists the formation of chromium complexes of higher basicity and so on. Although acid is released, the effect of the dilution is to decrease the concentration of hydrogen ions (an increase in pH value). This lessening of the hydrogen ion concentration is less than to be expected if no hydrolysis effects occurred. The effect on the basicity of the chrome salt is equally important since the tendency to the formation of Ol groups increases and with this the increase in molecular size on ageing and heating (Stiasny, *Gerberei-chemie*, p. 454 - 458). The astringency of the liquor also increases on dilution, in which respect chrome liquors differ from vegetable tanning liquors. This explains why it is not now customary to start chrome tanning in diluted chrome liquors, passing on to stronger liquors, although this was done in the early days of chrome tanning. Rather is the tannage started with liquors containing fair amounts of chromium and astringency is controlled in other ways, such as by adjustment of basicity or by the use of masking salts. Dilution, in affecting the basicity of the chrome salt, does not affect the basicity of the chrome liquor as a whole, the increase in free acid balancing the increase of the basicity of the chrome salt. Dilution also lessens the precipitation figure, which again denotes increasing astringency. If the chromium complex contains acid groups, then on dilution they are slowly displaced and their place is taken by water molecules, the chromium complex becoming more and more electropositive. This effect is very definite with basic sulphate liquors, is less with formiato chrome complexes but does not occur if the acid group within the complex is sulphite or oxalate, since these acid groups are not displaced by the water molecules.

In view of these manifold effects of dilution it will be evident that changes in the concentration of the chrome salt will be reflected in the tanning properties of the liquors and therefore in the properties of the leather produced.

With basic chromium chloride liquors, Gustavson (1926) found a steady increase in the uptake of chromium with hide powder with increasing concentration of the chrome salt in the case of liquors which were 12.8 per cent. basic, 33 per cent. basic and 54.6 per cent. basic. Thomas and Kelly (1921, 1922) found with chromium sulphate liquors that progressively increasing concentrations at first gave increasing and then a decreasing uptake of chromium. The position and sharpness of the maximum point in the uptake of chromium depended on the basicity of the chrome liquor. If chrome tanning were simply an electrovalent combination between chrome salt and collagen, involving a neutralisation of electric charges, then as dilution affects the nett charge on the chrome complex, when acid groups are present in the complex, an increasing concentration of kationic chrome liquors should involve an increase in the uptake of chromium and of anionic chrome liquors a decrease in the uptake of chromium. Wilson (*Gerberei-chemie*, p. 458) explains the maximum in the uptake of chromium

by the increase in the  $\text{SO}_4$  content of the chromium complex. Diluted chromium sulphate liquors contain chromium complexes which contain very little  $\text{SO}_4$ , but with increasing concentration the  $\text{SO}_4$  content of the chromium complexes increases and, consequently, the chromium uptake increases, but with the further entrance of  $\text{SO}_4$  anionic non-tanning chrome complexes are formed.

Stiasny, Küntzel and Kinzer (1934) showed that the maximum in the uptake of chromium in the case of chromium sulphate liquors is not due to case-hardening but is due to the penetration of acid groups into the chromium complex as a result of the increase in neutral salt content in the more concentrated solutions. The penetration of the acid groups lessens the positive charge on the complex chromium ion and the charge becomes increasingly negative. The lower the positive charge the greater is the equivalent of positively charged chromium required to neutralise the negative charges on the collagen. With chloride liquors there is no maximum in the chromium absorption because the chlorine ions do not enter the chromium complex to any appreciable extent. With a basic sulphate liquor containing no neutral salts the chromium absorption increases steadily with an increase in the concentration of chromium and there is no maximum point. The addition of neutral salt brings about the formation of a maximum point. They also point out that the pickling action of a chromium salt solution containing neutral salts increases with increasing concentration. This pickling action brings about a lessening in the swelling of the collagen, an effect which occurs at a comparatively low concentration and a decrease in its hydration, the latter effect requiring a comparatively high concentration. Sulphates have a much greater dehydrating action than chlorides, and it is suggested that the more dehydrated the collagen groups become the more handicapped are they in their ability to take up chromium. According to Elöd and Cantor (1934) the neutral salts depress the hydrolysis of a chrome tanning liquor, thereby reducing the amount of true tanning salts and also the membrane effect of the protein.

#### *(d) The Effect of Basicity.*

With increasing basicity, the astringency of a chrome liquor increases, the uptake of chromium is increased, the danger of over-tanning the grain increases and, in the later stages of tanning the attainment by the leather of the boiling test is quickened. Schindler and Klanfer (1929) pointed out that the chromium content of the grain layer with liquors of a basicity of over 40 per cent. is much greater than that of the middle portion of a leather and that this depends also on the age of the liquor, temperature of tanning and on the addition of sodium carbonate in the later stages of the tanning.

An increase in basicity brings about an increase in the number of OH groups in the chromium complex, increases olation (Stiasny, 1931, p. 458 - 460) and also causes an increase in the size of the chromium complexes (see Chapter VI). The rate of penetration of the chromium into the pelt is slowed up because of the increased size of the chromium complexes, the precipitation figure

is decreased, the pH value of the liquor increases and there is a corresponding decrease in the swelling power of the liquor. The relation between the pH value and the degree of olation has already been pointed out.

The most suitable basicity for practical purposes depends upon very many factors, such as the kind of pelt, the type of leather to be produced, previous treatment of the pelt, the nature of the processes after tanning, the kind and concentration of the chrome liquor, its content of neutral salts, and so on. According to Bergmann, Stather and Seligsberger (1929), the valuable properties of the natural hide are best maintained by tanning with medium basic liquors (about 33 per cent. basic). Chromium chloride liquors are less astringent than sulphate liquors for the same per cent. basicity, and it might be noted here that additions of sodium chloride to sulphate liquors tend to lessen astringency. Too low a basicity gives an empty, flat, hard, tinny leather with a tender grain. Too high a basicity overloads the fibres with tan and particularly the grain, resulting sometimes in a cracky grain and an undertannage of the middle layer.

#### *(e) The Effect of Additions of Neutral Salts.*

Chrome liquors prepared from chrome alum or dichromate contain neutral salts in solution, the minimum content being 1 molecule of neutral salt to 2 atoms of chromium. Chrome liquors which have been found in practice to be deficient in suitable neutral salts are generally given an addition of neutral salt. In the tannage of pickled goods this prevents acid swelling taking place in the tan liquors with the production of drawn grain. Apart from this action, which generally helps in the production of a lighter coloured leather with a finer grain (Stiasny, 1931), the addition of neutral salts to a chrome liquor affects the acidity and constitution of the chromium complex and, therefore, the tanning action of the liquor and the properties of the leather.

In considering the effect of neutral salts on chrome tanning, two aspects of the problem will be discussed, firstly the action on the chrome liquor and secondly the action on the pelt. Attention will be given to the type of salt added (sodium chloride, sodium sulphate, etc.), the type of liquor (chromium chloride or sulphate) and the concentration, basicity and degree of olation of the chromium complex.

#### *(a) The addition of sodium chloride to chromium chloride liquors.*

In 0 per cent. basic solutions, particularly on boiling and cooling, the addition of sodium chloride lowers the pH value and chlorine ions enter into the complex. With basic solutions, the pH value is generally lowered and the OH groups in the chromium complex prevent the entrance of chlorine ions. According to Stiasny, basic chrome chloride solutions always have their chlorine atoms outside the complex, even at 90 per cent. basicity, but according to Balanyi (communication to the Dresden Colloquium), on the addition of considerable amounts of salt to basic chromium chloride solutions, small amounts of chlorine ions enter the chromium complex. Gustavson (1925, 1927) goes still further

and states that the chromium complex in a basic chromium chloride liquor contains chlorine but this is less firmly held than the  $\text{SO}_4$  groups in sulphate liquors. This penetration of chlorine into the chromium complex must be coupled with an increase in pH value since the dissociation constants of the chloro salts are less than that of the hexaquo chloride. It is of note that if a dichloro-chromium chloride solution,  $[(\text{H}_2\text{O})_4\text{CrCl}_2]\text{Cl}$ , is made basic, then all the chlorine atoms within the complex wander outside it.

Small additions of salt, about 2 per cent. to a 56 per cent. basic liquor, cause an increase in the pH value of about 0.1, but with additions of 6 per cent. of salt and over, this effect is no longer evident. Similar effects have been observed on the pH value of hydrochloric acid solutions when sodium chloride is added. The increase in acidity is of practical importance since more acid will be taken up by the pelts. Many contradictory statements have been published as to the effect of additions of sodium chloride upon the precipitation figure of chromium chloride liquors. Wilson and Kern found that an increase occurred, whereas Gustavson found a decrease and Stiasny, using moderately basic pure chromium chloride liquors found only very slight alterations. Doubtless the previous history, the age and the composition of the chrome liquor are the disturbing factors. Highly basic liquors which have been boiled for some time give precipitates on the addition of sodium chloride. Liquors made basic with sodium hydroxide or sodium carbonate, pure chromium chloride liquors and commercial liquors all behave differently. The effect of additions of sodium chloride upon the chromium uptake is also of practical importance, and it would appear that pH changes are only of secondary importance. Using a 48 per cent. basic liquor, Gustavson (1927) found a greatly increased uptake of chromium with liquors of low concentration but this action disappeared at a concentration in the chrome liquor of 3.4 per cent. of chromium and was reversed above that concentration (*i.e.*, the uptake was lessened). This last effect is probably due to too great an increase in particle size and colloidal character which occurs when sodium chloride is added to highly basic liquors, even to the point of bringing about precipitation. From a practical standpoint, a chromium chloride liquor, after the addition of sodium chloride, gives as full a leather as sulphate liquors. The tannage is commenced with a medium basic (30—45 per cent.) chloride liquor which contains enough salt just to hinder swelling. The salt content can then be increased up to 6 per cent. on the liquor. The final stages of the tanning are accelerated by the addition of alkali.

( $\beta$ ) The addition of sodium sulphate to chromium chloride liquors.

The effects produced are more pronounced and of a different kind from those when sodium chloride is added. The pH value is lowered according to Stiasny (*Gerbereichemie*, p. 463). The precipitation figure is lowered as chromium sulphates are formed which, at the same basicity, precipitate more easily than the chloride. The addition of sodium sulphate precipitates chromium chloride liquors if their basicities are over 60 per cent.

The addition of sodium sulphate alters the composition of the chromium complex, due to the strong tendency of the  $\text{SO}_4$  group to enter the complex; the liquors take on the tanning properties of chromium sulphate liquors and the astringency of the liquor is

Gustavson (1923) gives a tanning method by which the tannage, using a chloride liquor, was increased, not by the usual addition of alkali, but by the addition of sodium sulphate during the process, taking care to avoid precipitation (see below). The tannage can be started with very basic chromium chloride liquors, which, because of the small complexes, penetrate very readily. The later addition of sodium sulphate leads to the formation of large chromium complexes of high tanning value but with the chromium already evenly distributed throughout the skin. In practice, it is better to add aluminium sulphate to highly basic chloride liquors rather than sodium sulphate. The aluminium sulphate retards precipitation and gives a fuller leather. Care must be taken not to add too much aluminium sulphate or it will be found difficult to get good blacks.

( $\gamma$ ) The addition of sodium chloride to chromium sulphate liquors.

The basicity is lowered by this addition and the pH value is raised. It increases the precipitation figure, a change which, according to Stiasny (1931), is dependent on the previous history and composition of the liquor; it does not affect the chromium complex unless the chlorine ion concentration is great, when there is some interchange of  $\text{SO}_4$  and Cl in the chromium complex (Schindler and Klanfer, 1928; Hudson, 1927); it lessens the swelling action of acid introduced in the pickled goods, causes an increased uptake of acid by the pelt, thereby retarding and lessening the uptake of chromium, an effect which is desirable in the early stages of tanning and leads to the production of a flexible, fine clear grained leather, suitable for colours (see Burton, 1920 - 23).

According to Wilson and Gallun (1920), the addition to chrome liquors of sodium chloride or ammonium chloride, which can be present in a skin bated with an artificial bate, lessens the rate and extent of combination of chromium. With larger amounts of these additions, 1 g. molecule of either salt per litre, that is, about 6 per cent. of salt or 5.5 per cent. of ammonium chloride, the product resulting after 24 hours' tanning in a chrome liquor containing 1.7 per cent.  $\text{Cr}_2\text{O}_3$  will not stand the boiling test.

The use of too much salt gives a flat, hard, tinny, unsatisfactory leather and it is one of the important practical factors in chrome tanning to adjust the salt content to its most satisfactory amount. This can best be done as the result of practical experience (Stiasny, 1931), as it depends on so many factors, such as concentration, basicity and composition of the tanning liquor.

( $\delta$ ) The addition of sodium sulphate to chromium sulphate liquors.

The addition raises the pH value and lessens the uptake of chromium and acid by the pelt. According to Wilson and Kern (1917) the precipitation figure is increased, but results in this field, as in the case of addition of sodium chloride, are contra-

dictory and depend upon the nature of the chrome liquor. In a recent paper by Stiasny and Ziegler (1933) explanations are given for the behaviour of different chrome liquors towards sodium chloride and sodium sulphate. An addition of sodium sulphate affects the chromium salt in that  $\text{SO}_4$  enters the complex, thereby reducing the nett positive charge on the kationic chromium and eventually leading to the formation of negatively charged anionic chromium complexes. This is pronounced in strongly basic liquors and liquors prepared hot if a fair amount of sodium sulphate be added. A reduction in the rate of combination of protein and tan may also be due to some displacement of OH from the complex ion, which may occur by mass action, thereby rendering the chromium complex less basic and lessening the tendency to form more highly co-ordinated complexes by olation. On dilution and standing, the  $\text{SO}_4$  group is displaced by water from the complex, thus restoring its electropositive nature. Moderate additions of sodium sulphate lead to the production of a full leather of good stand (Burton, 1920 - 23). The chromium complex taken up by the hide in the presence of sodium sulphate contains more  $\text{SO}_4$  groups than if sodium sulphate is not present. All these factors are so inter-related as to present an extremely complicated state of affairs.

(e) The addition of aluminium salts to chrome liquors.

A combination tannage of chromium and aluminium is specially recommended by Gustavson (1923). The addition of a 33 per cent. basic aluminium sulphate to a 40 per cent. basic chromium sulphate solution gave a 74 per cent. spending of the chrome bath as against 62 per cent. without the aluminium sulphate. The tanning was more rapid and the leather improved. The addition raised the precipitation figure of the liquors.

Aluminium salts may also be added to highly basic chromium chloride liquors with advantage if the addition is made after the early stages of the tannage are completed (Stiasny, 1931). They act in a similar manner to sodium sulphate, converting the basic chromium chloride into less soluble chromium sulphates and at the same time beneficially affect the tannage, an effect which Gustavson attributes to the formation of mixed chromium aluminium complexes. 33 per cent. basic aluminium sulphate liquors (Gustavson, 1926) differ from chromium sulphate liquors of the same basicity in that pre-treatment of the pelt (hide powder) with neutral salts increases the uptake of aluminium without affecting the uptake of chromium. The chromium uptake is only similarly affected in the case of anionic chromium complexes or very highly basic liquors.

As mentioned earlier, the addition of neutral salts can be considered as affecting the chrome liquor or as affecting the material being tanned. The possible effects on the pelts have a great practical importance since before and during chrome tanning these are subjected to the action of alkalies, acids and salts. This field is also of great theoretical interest in the light it throws on the mechanism of chrome tanning. It will thus be referred to again in Chapter VII, which deals with theories of chrome tanning.

The action of neutral salts on pelt before tanning can be divided into swelling effects and those which, for the purpose of this review, can be classified generally under the term "salt" effects. For example, Thomas and Foster (1925) found that chlorides have a stronger disintegrating effect on hide powder than sulphates. McLaughlin and co-workers (1929) found that unsalted hides require more intensive wet-work treatment than wet-salted hides unless the unsalted hides are soaked in liquors containing salt. Dried hides also will behave like salted hides if soaked in a 10 per cent. salt soak.

This "salt" action of neutral salts increases with temperature and concentration. In the case of sodium sulphate and magnesium sulphate, the "salt" actions are less than that of water.

Mixtures of neutral salts sometimes act antagonistically, for example, the "salt" action of sodium chloride is strongly depressed by additions of sodium sulphate. Gustavson (1926) followed these "salt" actions on pelt further and studied their effect on the subsequent chrome tannage of the pre-treated pelt. There was very little effect on the uptake of chromium when medium basic kationic chromium complexes were used but very definite effects were produced with (1) chrome liquors containing both kationic and anionic complexes, (2) chrome liquors containing only anionic complexes.

The effect of liming is also of interest. Gustavson and Widen (1926) found that an increased period of liming brought about an increase in the uptake of chromium both for kationic and anionic liquors. Bating acts similarly to liming but the action of the liming process is often much greater than that brought about by the action of neutral salts. In ordinary chrome tanning, treatment with sodium sulphate and salt in the pickle operation would have comparatively little effect on kationic chrome complexes and little more on anionic chrome complexes.

(f) *Temperature.*

A rise in temperature increases hydrolysis, the amount of free acid, the degree of olation, the molecular size and hence increases the astringency of a chrome liquor. According to Stiasny (*Gerbereichemie*, p. 470) it would, therefore, appear advantageous to start the tannage cold at about 22 - 25°C. and finish it warm at about 42°C., taking care that intermediate temperatures are not sufficiently high to cause damage to untanned portions of the pelt. This procedure brings about a better exhaustion of the tanning liquor. A rise in temperature affects liquors made basic with sodium carbonate. A displacement of the CO<sub>3</sub> groups by OH groups increases the basicity and astringency of the tan. Thus many factors have to be considered in a study of the effects of increases of temperature upon chrome tanning.

(g) *Time Factor.*

The rate of uptake of chromium is most rapid in the very early stages and then steadily decreases.

(h) *The Effect of Additions of Masking Substances to the Chrome Liquors.*

According to Stiasny (1931), chrome liquors which contain chromium salts with organic acids such as the formate and oxalate

are characterised by being only very slightly astringent. They are thus very suitable for tannage of the grain. Such liquors are easily prepared by the addition to a chromium chloride or sulphate liquor, of a suitable basicity, of the alkaline salt of an acid which shows a special tendency to complex formation with the chromium atom. For example, the addition of sodium formate or oxalate or sulphite or mixtures of these gives tan liquors of greatly altered properties, depending upon the amount of the added material.

Such additions are said to mask the chromium salts since they inhibit to a greater or less extent the characteristic precipitation reactions of the chromium ion and if enough be added, the tanning action of the chrome liquor is entirely prevented, but with intermediate amounts the effect is to mellow the tannage. This masking process renders a chrome liquor stable towards precipitating agents such as alkali, ammonia and so on. In many cases, the complex chromium ion becomes electronegative. Masking substances are sometimes formed in the preparation of one-bath chrome liquors, particularly when dichromate is reduced by organic substances, for example, glucose. The effect is, however, likely to be much less regular than that obtained by adding a definite amount of the masking material to the chrome liquor. Measurable masking occurs on the addition of a suitable salt in the cold but in most cases the change is accelerated by heating. The masked tan liquor gives a fine grain and the danger of over-tannage of the grain is reduced. The tannage of bated pelts can be started in such liquors without an intermediate pickling and followed up and completed rapidly by the use of an ordinary basic chrome liquor without detriment to the fineness of the grain. The tanning action of a masked chrome liquor depends upon the amount of masking, the basicity and the method of preparation. The degree of masking depends upon the amount of masking substance compared with the amount of chromium. For example, according to Stiasny and Szegő (1926), sodium sulphite additions ( $>0.5$  mol. sulphite per 1 Cr) are masking and give anionic chromium complexes which tan satisfactorily. The addition of 1 mol. of sodium oxalate to a liquor containing 1 mol. of 33 per cent. basic chromium sulphate, gives a solution in which the chromium complex is completely anionic. The basicity of such liquors is taken as the basicity before masking. It is also of importance whether the masking substance is added to the cold chrome liquor or the change conducted hot (sulphite additions must be in the cold otherwise precipitation occurs), whether the alkali (sodium carbonate) is added to the chrome liquor before or after the masking substance and so on.

From many laboratory experiments, Stiasny (*Gerbereichemie*, p. 474) using 0 per cent., 33 per cent. and 50 per cent. basic sulphate liquors and 0.5—2 mol. masking salt (sodium oxalate, formate, sulphite) per one atom of chromium, found that additions of either oxalate or sulphite gave a tight grain and a firm leather, although a mixture of oxalate and sulphite together gave an unexpectedly hard leather.

The use of more than 1 mol. sulphite affected the dyeing of the leather. Formate liquors ( $>1$  mol. formate) gave soft leather with a spready grain and a higher shrinkage temperature than

the oxalate or sulphite liquors. Each masking substance produces its own effects so that almost any desired effect can be brought about by suitable additions to the chrome liquors. Satisfactory masked sulphate liquors for starting a tannage were obtained by adding 0.5 mol. oxalate, plus 0.5 mol. formate, or 1 mol. formate plus 0.5 mol. sulphite, or 0.5 mol. formate plus 0.25 mol. sulphite. The tannage was continued and completed using a 50 per cent. basic glucose-reduced liquor. It is advisable to delime pelts before giving them a tannage with a masked chrome liquor.

The preliminary use of masked chrome liquors should give chrome leathers which in the fineness of their grain very closely resemble leathers produced by the two-bath process of chrome tanning.

According to Stiasny (1924 - 26), see also Wilson (1929) p. 687, pre-tannage with chromiates (containing anionic chromium complexes) gives a leather with a finer break, a fuller feel and tighter flanks on completing the tannage in the usual way.

Some information is given in Chapter VI as to the effect of additions of masking substances upon the molecular size of basic chrome tanning salts.

Another type of masking has already been described under the account of the preparation of liquors.

The presence in chrome liquors of certain organic hydroxy acids or salts thereof, not only retards but even reverses chrome tanning (a dechroming action). The best known of these is Rochelle salt (potassium sodium tartrate). The following also have similar effects: sodium citrate, lactate, gallate and salicylate. The reversing effect is attributed to the formation of complex chromium ions. According to Procter and Wilson (1916), a small amount of these substances does not prevent tanning but produces a fullness and softness in leather not otherwise attained. Excess glucose has this effect and probably small amounts of Rochelle salt would produce the same effect. A very small amount of Rochelle salt would give a fuller feel and a thicker and plumper leather. The addition of a small amount of hydroxy compound, such as tartaric or lactic acids, gives a full and soft leather.

By the use of dechroming agents, it can be shown that the chrome tanning process is a reversible process under certain conditions. The process of dechroming has been used practically in the production of glue and the recovery of chromium from chrome leather waste and for the stripping of chrome from the surface of chrome leather which is to be re-tanned with vegetable tanning materials. Rochelle salt can also be used for overcoming chrome case-hardening. On the basis of the Werner concept, the peculiar action of tartrates is due to the vigour with which the anion tends to penetrate the chromium complex, displacing other co-ordinated groups.

#### SUMMARY.

1. The astringency of chrome tanning liquors depends on the nature of the chromium salt. Chromium sulphate liquors are more astringent than chromium chloride liquors, and both of these are more astringent than liquors made by the reducing action of organic compounds.

2. Astringency is affected by basicity, the more basic liquors being the more astringent. Hence liquors with very low pH values are less astringent than liquors with higher pH values. Pickling before tanning helps to mellow the tannage.

3. Raising the temperature of a chrome liquor increases its astringency, probably through increase of olation. Diluting a chrome liquor does not reduce its astringency. The more astringent the liquor the greater is the fixation of chromium by the collagen.

4. Salts influence the character of a chrome liquor by the mass action effect of their ions; *i.e.*, sodium chloride may reduce the astringency of an  $\text{SO}_4$  liquor, sodium sulphate may increase the astringency of a Cl liquor. Hence salt (NaCl) pickles are preferable to alum or other  $\text{SO}_4$  pickles. Salts also have a physical effect by reducing the plumping induced by acid liquors.

5. For good grain and full leather, the tannage should be mellow at the start and astringent at the finish. Hence, the tannage should start in organically reduced liquors of low pH, moderate salt content (to check plumping) and moderate temperature.

6. Chrome liquors made by reducing dichromates with glucose or other organic materials give a softer fuller leather than those made by reducing with sulphur dioxide or sulphites. This is probably due to the nature of the acid groups penetrating the chrome complex, and the extent to which they displace water groups.

### CHAPTER III.

#### SOME FACTORS IN THE TWO-BATH CHROME TANNING PROCESS.

##### PRACTICAL PROCEDURE.

THE system of chrome-tanning which is most frequently adopted for glazed kid manufacture is that known as the Two-Bath Process. As usually carried out, this variation of ordinary chrome tanning consists in impregnating the puered and/or pickled skins with a solution of chromic acid and salt. When the absorption of chromic acid ceases, the goods are removed, freed from superfluous liquor, and then treated with a solution of sodium thio-sulphate ("hypo"), and hydrochloric acid. This leads to the production of a green basic chromium salt directly on the fibres.

The details of the process employed in different yards may vary, but the process remains essentially as stated above.

##### (a) FIRST BATH.

The principle involved in the First Bath is an even absorption of chromic acid by the goods to an extent sufficient to produce 3—4 per cent. chromic oxide in the final leather. The chromic acid is always prepared by the action of a mineral acid, generally hydrochloric acid on a solution of sodium dichromate.

As now worked it is quite a simple process, the only skilled part of the operation being the weighing of the goods, the dichromate and the acid.

But several variations in the details of the process can be made the effect of which will now be considered under the following headings:—

- (1) The amount of dichromate used for 100 lbs. of goods treated.
- (2) The proportion of acid to dichromate.
- (3) The concentration of the liquor and the manner in which it is added.
- (4) The addition of salt.
- (5) Temperature.
- (6) Time and penetration of the fibres.
- (7) Utilisation of spent liquors.
- (8) Horsing-up.
- (9) Light.
- (10) Striking-out.
- (11) Dipping.

(1) *The Amount of Dichromate used for 100 lbs. of Goods Treated.*

This varies from 5—7 lbs. for every 100 lbs. of the scudded lt.

If the goods are properly reduced in the Second Bath there is no need to use as much as 7 per cent. dichromate, and any quantity above 6 per cent. is wasted. The use of 7 per cent. does not necessarily imply that more chromium is retained by the tanned or finished leather. This factor of chrome retention is governed by the system adopted in the Second Bath. For example, certain goods chromed with 6 per cent. dichromate produced a leather containing 4·8 per cent. chromic oxide, whereas the leather from another load of goods chromed with 7 per cent. dichromate showed only 2·7 per cent. of chromic oxide.

There is a certain optimum proportion of chromic acid to pelt which ensures that the pelt absorbs the greatest percentage of the chromic acid used. This proportion has been found to be 2·85 lbs. pure chromic acid for every 100 lbs. of scudded pelt. If more than this proportion is used, although the total amount absorbed by the pelt is more, the proportion of chromic acid absorbed to that unabsorbed is less. This is illustrated in the following table:—

TABLE I.

lbs. Chromic acid per 100 lbs. pelt.	lbs. Chromic acid absorbed per 100 lbs. chromic acid used.	lbs. Chromic acid left in the solution per 100 lbs. chromic acid used.
0·3	70	30
2·85	76	24
3·9	68	32
4·9	59	41

2.85 lbs. chromic acid correspond to 4.3 lbs. dichromate, which is slightly less than that used in trade practice (5—7 lbs.). The percentage of chromic acid taken up by a pack of goods does not reach 76 per cent. in practice because of the presence of salts which decrease the amount to about 66 per cent.

(2) *The Proportion of Acid\* to Dichromate.*

In practice this proportion is usually 1 : 2, i.e., 3 lbs., commercial hydrochloric acid to 6 lbs. dichromate. Little attention, however, appears to be given to the strength of the acid used. This should not be overlooked, since it may vary from 23 to 36 lbs. actual HCl per 100 lbs. of the commercial acid (16—22° Bé), the remaining 77 to 64 lbs. being water.

The chemical equivalent of dichromate and acid is shown by calculation to be as follows:—

6 lbs. dichromate is equivalent to  $4\frac{1}{2}$  lbs. hydrochloric acid (83 per cent.).

As is well-known, the usual trade proportion of 2 : 1 gives an excess of dichromate over the chemical equivalent of acid. The surplus dichromate is said to function as a safeguard against accidental excess of acid and as a regulator of the rate of absorption of chromic acid by the pelt. It has often been stated that any other salt would serve this purpose equally well, and since dichromate is expensive it is suggested that the excess of dichromate is unnecessary and should be replaceable by common salt with equally satisfactory results.

Experiment does not confirm these views. If pelt is agitated in a solution containing hydrochloric acid and dichromate in equivalent proportions, instead of absorbing only chromic acid and leaving sodium chloride in solution, the pelt absorbs hydrochloric acid along with some chromic acid and leaves unchanged dichromate in solution; as a result less chromic acid is absorbed by the pelt than if an excess of dichromate had been used over and above the chemical equivalent. Therefore, the suggestion to replace the excess of dichromate with common salt is not in accordance with modern views.

In practice the proportion of acid taken is much less than the equivalent, but the ready absorption by the pelt of chromic acid from trade liquors can be explained as follows:—

At the beginning of drumming the pelts absorb the hydrochloric acid more rapidly than the chromic acid. As drumming proceeds the chromic acid displaces the hydrochloric acid from its unstable combination with the pelt, and itself combines with the pelt to form a much more stable compound. This process continues until all the hydrochloric acid in the pelt has been replaced by chromic acid (Innes, 1935) (see also below).

In cases where pelts have previously been pickled, they may contain almost all the acid of the pickling liquor. Consequently,

\* In this section "acid" will always refer to commercial hydrochloric (muriatic) acid containing 83 per cent. hydrochloric acid (sp. gr. 1.170).

in making up chromic acid liquors, full allowance should be made for the amount of acid used in pickling. (One lb. by weight of sulphuric acid of 95 per cent. strength is equivalent to 2.15 lbs. of hydrochloric acid of 33 per cent. strength.)

(3) *The Concentration of the Liquor and the manner in which it is added.*

Even in the absence of light, if too strong a solution of dichromate be used there is a danger that the skin fibres will be oxidised and thus damaged. The use of a diluted liquor greatly lessens this risk, and does not greatly affect the amount of chromic acid absorbed by the skin. The extent of dilution is, of course, limited by the capacity of the drum.

A suitable volume of liquor to employ at the beginning of drumming is about 20 galls. per 100 lbs. of scudded goods. A solution containing 6 lbs. of dichromate, 3 lbs. of commercial hydrochloric acid (33 per cent.), and 1 lb. of salt in 20 galls. of water has a sp. gr. of 1.025 (8½°Bé).

A procedure often adopted in practice in the case of goods which have not been pickled is to add water to the drum-load of pelts sufficient to float them freely (about 10 galls. per 100 lbs.), and to add a more concentrated chromic acid liquor containing the amounts of dichromate, hydrochloric acid and salt given above. This strong solution is added in 2 to 3 portions at intervals of about 30 or 20 minutes. After the last addition the total volume of liquor in the drum is then 20 galls. per 100 lbs.

When pickled goods are being chromed, it can be arranged that the final pickle liquor has a volume of about 10 galls. per 100 lbs.

(4) *Addition of Salt.*

It is not uncommon in trade practice to add 1 lb. of common salt to every 6 lbs. of dichromate. It is claimed that the addition of salt prevents drawn grain. It appears, however, that no account is taken of the salt produced by the action of the hydrochloric acid on the dichromate, 3 lbs. of acid producing over 1½ lbs. common salt. Furthermore, goods which have been pickled contain considerable amounts of salt, so that further additions of salt to the chromic acid liquor seems superfluous. Moreover, it has been shown (Innes, 1935) to decrease the uptake of chromium.

(5) *Temperature.*

As pointed out under (3), chromic acid liquors have an oxidising action on skin. This is considerably increased when the temperature is raised, and if the temperature is too high, *e.g.*, 90°F., the leather will be very tender. Atmospheric temperature should not be exceeded.

(6) *Time taken for Penetration of the Fibres.*

The goods absorb their full amount of chromic acid during the course of 4 hours' drumming. To ensure even absorption drumming should be continued till at least 2 hours have elapsed from the commencement of drumming. The drum may then stand overnight and be run for the remaining 2 hours next morning. Goods should remain at least 4 hours in the liquor, and even then the chromic acid solution may still continue to penetrate the fibrils of

the skin more thoroughly. But little is really known on this point. The so-called hardening action of a solution of dichromate on skin also requires detailed investigation.

(7) *Utilisation of Spent Liquors.*

Attempts have been made by tanners to recover the considerable amounts of sodium dichromate which remain in the spent chromic acid liquors. This has, however, not developed into a universal and regular practice, because complete success depends on a somewhat careful chemical control, which is not worth while owing to the small amount of dichromate recovered. An examination of a used works liquor showed about 44 lbs. of dichromate left over after tanning a 2,000 lb. load of goods.

(8) *Horsing-up.*

It has been suggested that this is a very necessary operation which ensures more complete penetration of the solution into the fibrils, where the chrome becomes fixed, thus preventing subsequent bleeding during treatment in the second bath. No information is at present available as to the time taken for complete penetration, if it can actually occur. Neither is it known whether such fixation is accompanied by a partial destruction of the fibres.

(9) *Light.*

During drumming the goods are protected from the action of light. It has been stated that light has a detrimental effect on goods containing chromic acid, and in practice the horsed-up goods are covered with bags in order to shield them from the light. Recent experimental work, however, has shown that light is without appreciable effect on either the uptake of chromium or the ease with which it can be removed by water extraction.

(10) *Striking-out.*

There are two advantages to be gained by squeezing out the superfluous liquor from the goods after the first bath:—

- (a) Less acid will be required in hypoing.
- (b) The grain of the skin is flattened and any creases are removed.

The substances in solution in the expressed liquor consist mainly of dichromate and salt, neither of which would be absorbed by the pelt even if it were left in for weeks. It is stated that the pressure employed should not be too great, as otherwise chromic acid solution may be expressed. This seems somewhat unlikely, and lacks experimental proof.

(11) *Dipping.*

The process of dipping chromed goods one by one in an acid solution of hypo is said by some to prevent the diffusion of the chromic acid ("bleeding") from the skins into the second bath.

It is more likely that this bleeding is a diffusion of unchanged sodium dichromate from the grain and/or flesh surfaces. In whatever form the chromium thus lost may be, it will be easily re-absorbed on to the grain and/or flesh surfaces of the pelts if the process of hypoing is properly controlled.

### ( $\beta$ ) SECOND BATH.

As is well known, the second bath consists of a solution of "hypo" containing acid. In this solution the chromed skins are paddled, the orange chromic acid they contain thereby becoming reduced to the bluish-green basic chromium compound.

The objects to be aimed at in the second bath are two-fold:—

- (1) The complete reduction of all the chromic acid in the skin.
- (2) The formation and fixation of a chromium compound of the correct basicity in the leather.

These objects can be achieved with certainty if the proportion of acid used during the process is carefully controlled, and if the amount of hypo used is sufficient to ensure an adequate surplus being left unused at the end.

Although complete reduction of the chromic acid is almost invariably effected, the formation of the chromium compound of the correct basicity is not always achieved in glazed kid factories. It will be shown how the leather is affected if insufficient attention is paid to this point, and also how the best tannage can be attained.

The following will now be considered:—

- (a) Proportion of hypo to goods.
- (b) Proportion of goods to liquor.
- (c) Proportion of acid used and the method of feeding.
- (d) Temperature.
- (e) Period of action.
- (f) Suggestions for a standard method of hypoing.

#### (a) *Proportion of Hypo to Goods.*

This varies in different yards from 16—25 lbs. of hypo to every 100 lbs. of scudded pelts. The proportion which should be used depends to a considerable extent on the amount of dichromate which has been used and also to a lesser degree on whether the skins have been previously dipped.

For instance, if the proportion of dichromate to goods was 6 per cent., and the goods have not been dipped, the proportion of hypo which is adequate and at the same time not wasteful is 20 lbs. per 100 lbs. pelt. At the end of the process, when the goods are removed, there should still be not less than 3 lbs. of hypo left unused. If there is less than 3 per cent. there is a risk that the goods will not stand the boiling test. A cutting which has been satisfactorily tanned will not appreciably shrink or curl. It is, of course, well-known that the boiling test is not an infallible guide to the quality of the leather finally obtained. If, on the one hand, the goods have not been well prepared for tanning, *i.e.*, the fibre structure is imperfectly opened up, correct tannage as indicated by the boiling test will not ensure that they will become first-class leather. If, on the other hand, the fibres of the pelt have been properly separated during soaking, adequately plumped during liming, and efficiently puered, special conditions for hypoing need not perhaps be so rigidly adhered to and yet a good leather will be obtained. But at the same time, such skins would produce still more mellow leather if hypoing were carried out along the lines indicated below.

(b) *Proportion of Goods to Liquor.*

The proportion of goods to liquor in the hypo paddle may vary within fairly wide limits. If too large a pack of goods be used, they will jam in the paddle so that they cannot be reduced evenly. If too small a pack is treated, there is a tendency for the hypoed goods to fail under the boiling test, the failure being probably due to the concentration of the hypo in the liquor being too low.

The following figures may be taken as a guide:—

In a paddle of 800 gallons capacity, packs of 800—1200 lbs. can be tanned satisfactorily. A pack of 600 lbs. would possibly be too small and would be liable to fail under the boiling test. Packs over 1200 lbs. in weight will as a rule become jammed during paddling.

(c) *Proportion of Acid employed and the Method of Feeding.*

The actual procedure employed from yard to yard varies considerably.

(1) In some cases sufficient acid (up to 13 per cent.) is used to maintain a considerable excess of sulphur dioxide at all stages from start to finish.

(2) In others, a fixed amount of acid is used which is equal to half the weight of the hypo. Sometimes the actual strength of the acid and, therefore, the actual proportion of acid to hypo is not known.

Although in some cases the amount of actual hydrochloric acid used is somewhat less than that employed in (1) above, it is still more than sufficient to ensure complete reduction.

(3) In yet other cases the amount of acid added is kept down to a minimum so that there is always only a slight amount of acid in excess of that necessary to ensure the reduction of all the chromic acid coming into the solution from the skins. Furthermore, in such cases, although the addition of acid towards the end of the process is carefully watched, the initial amount may vary from 2 to 5 lbs. of commercial acid per 100 lbs. of goods.

In this method, if 20 per cent. of hypo is used, the amount of acid required is generally below 8 per cent. of the weight of the goods.

It has been found that the lower the initial amount of acid added the softer will be the grain of the finished leather.

(d) *Temperature.*

Some little attention should be given to this question, since goods may be damaged if hypoing is carried on outside a certain range of temperature. Cases have been known where full packs have been hypoed in a liquor at as low a temperature as 37°F. Reduction was very slow, the tanned goods failed under the boiling test, and when finished the leather felt very tinny and undertanned. No examples in practice can be quoted where hypo liquors have been heated above summer temperature (65°F.), but it is generally felt that in the early stages, tannage would be far too rapid at higher temperatures and that in extreme cases there would be destruction of fibre-substance by the oxidising action of the un-reduced chromic acid, with consequent tenderness of the finished leather.

The best results are obtained at an initial temperature of 55°–60°F. As hypoing proceeds the temperature will rise a further

6° or 7°. When the goods are fully tanned (at the end of the process) the liquor may be safely heated up. This would accelerate the ageing of the leather, which probably need not then undergo the usual process of lying in pile for several days.

(e) *Period of Action.*

As carried out by the process described below under (f), complete reduction is effected in about 2 hours. Cases have been known where a much longer time than this has been necessary, but these are exceptional and require investigation.

Hypoing should be started so that about 2½ hours paddling can be carried out without interruption. If necessary, paddling can then be stopped, although the longer it can proceed up to 4 hours, the better. Hypoed goods should always be left in their liquor over-night and given at least half an hour paddling next morning. They should then stand the boiling test.

(f) *Suggestions for a Standard Method of Hypoing.*

The limits of safety given above for the various factors involved in hypoing may now all be exemplified by describing the whole process in detail.

For purposes of illustration the case will be considered of a load of 1000 lbs. of goods which have been chromed with 6 per cent. dichromate, but have not been dipped before being struck out. The following procedure is recommended, the acid employed being of 33 per cent. strength (sp. gr. 1.170 or 21° Bé.):—

Twenty per cent. (200 lbs.) of hypo are completely dissolved in hot water and diluted with water in a paddle of about 300 gallons capacity, so that the temperature of the bath is finally between 55° and 60°F. As soon as the goods are ready for entering, the reel is started, 2 per cent. (20 lbs.) of acid is added, and the bath well plunged up. When the liquor becomes milky (the warmer the liquor the quicker this occurs), the skins are entered without delay, about half a dozen at a time. As the colour of the solution gradually changes to a yellowish tint, 5 lbs. (½ per cent.) of the acid are added, being evenly distributed to avoid local excess, and further similar additions are made as required till the amount of acid which has been added reaches 60—65 lbs. Subsequent additions should be made in quantities of 2½ lbs. at a time until reduction is nearly complete.

At this stage it is somewhat difficult, especially in a bad light, to discern whether the green colour of the liquor has changed to a yellowish green. This is best shown up by comparing the tints of two samples of the liquor placed in two colourless glass cylinders (not greater than 1 in. internal diameter), to one of which a few drops of acid have been added. If there is no difference in tint, no further addition of acid to the paddle is necessary. Also, if there is only a slight difference in tint, no addition of acid may be required as reduction appears to continue and the liquor loses the yellowish tint in the course of half an hour or so. If, however, the yellowish tint deepens it can be discharged by the addition of quite a small amount of acid, ½—1 lb. being probably sufficient.

This stage is generally reached in about 1½—2½ hours, depending on the substance of the skins and the temperature of the bath.

Paddling should be continued for at least a further  $\frac{1}{2}$ —1 hour before stopping the reel.

The liquor should now be tested by means of an indicator to see whether it contains an excess of acid. A few drops of a 0.1 per cent. solution of methyl orange are added to about 25 c.c. of the liquor, when, in the absence of excess acid, a yellow solution is obtained. If a red colour develops, too much acid has been added. In this case, very small amounts of soda should be carefully added until the addition of methyl orange to a test portion of the solution does not give a red colour.

As soon as the liquor has acquired the correct acidity, the green colour gradually becomes lighter, due to the re-absorption of the chromium by the goods. The goods should not be removed from the liquor until about 18—20 hours have elapsed since they were entered. By this time the colour of the liquor should be a very pale green and may indeed often be colourless.

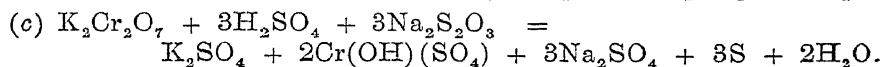
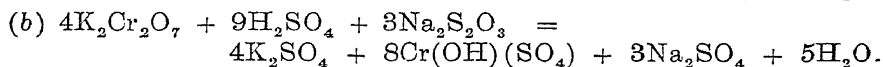
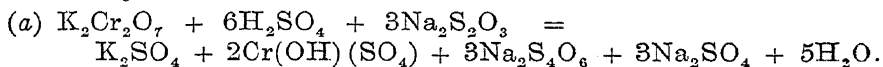
When the goods have had their full time, they should be removed from the liquor and left in pile for periods varying from 2 to 7 days.

The minimum period for which the goods should remain piled is not known, and the changes which take place during this time are not fully understood. As suggested above, it appears possible to accelerate the ageing of the goods by raising the temperature, and it is probable that the warmer the spent liquor the shorter is the time necessary for goods to lie before being ready for the next process (washing).

#### THE CHEMISTRY OF THE TWO-BATH CHROME TANNING PROCESS.

The underlying idea which is the basis of the two-bath process is that by impregnating the skins with a solution of chromic acid and then reducing this to the basic chrome tanning compound, the latter is formed where it is required, namely, directly in contact with the collagen fibres. The chemistry of the reduction of chromic acid or alkali dichromate to basic chromium salt has generally been inferred to be the same as the chemistry of the reduction of dichromate that occurs when the same re-agents are used in making the one-bath chrome liquor. It must be borne in mind, of course, that the conditions of the reduction of the (sodium) dichromate to basic chromium salt in the two-bath process are different from those that occur in making a one-bath tan liquor, since the concentration of the reducing agent is less and the temperature is considerably lower. The course of the reduction in the two-bath process has been fully studied by Stiasny and Das (1912).

Stiasny and Das showed that mixtures of dichromate, thio-sulphate and sulphuric acid can react at room temperature in three ways:—



Dilution, whilst decreasing the speed of reaction, increased slightly the proportion of reaction (a), decreased considerably the proportion of reaction (b), and increased considerably the proportion of reaction (c). An excess of acid increased the speed of reaction, increased the proportion of reactions (a) and (b) and decreased considerably the proportion of reaction (c). An excess of thiosulphate increased the speed of reaction at the beginning but retarded complete reduction. It increased the proportion of reaction (a), decreased the proportion of reaction (b), and increased considerably the proportion of reaction (c).

In practice, very little sulphur is produced: that formed in reaction (c) is reacted upon by the tetrathionate to form pentathionate. Any sulphur produced in practice is probably due to the direct action of acid and basic chromium salts on the thiosulphate.

Allowances must also be made for the presence during reduction in the two-bath process of another factor, absent during reduction in the preparation of a one-bath liquor, namely, the collagen fibres. Untanned collagen fibres are far from playing an inert role in any acid solution. The chemistry of the first bath of the two-bath tanning process has been investigated by Innes (1935). He observed that goods dried out after treatment in the first bath had become leathered, in other words, the first bath exercises a definite tanning action on pelt. This leathering of the pelt does not occur until a certain amount of chromium has been fixed by the skins. The fixation of the chromium is favoured by mechanical treatment and the chromium once fixed is not readily removed by washing with water. The leathering action of chromic acid on pelt is also readily observed in laboratory experiments where pure chromic acid solutions have been used. In these cases mechanical treatment is unnecessary.

Innes is careful to point out that at present there is no evidence that the leathering of the pelts in the "yellow" is an essential stage in the production of satisfactory "blues," though there is no doubt that leather in the "yellow," and the production of a good "blue," both depend on the fixation of sufficient chromium.

Chromic acid is absorbed by pelt from its solutions in proportion to its concentration. From solutions containing sodium dichromate and hydrochloric acid, the absorption of chromium increases with the increase in the ratio of hydrochloric acid to dichromate present. When these are present in chemically equivalent proportions there is a greater absorption of chromium by the pelt per unit of chromium in solution than there is at the ratio of hydrochloric acid to dichromate generally used in trade practice. The addition of sodium chloride to any solution containing chromic acid leads to a decrease in the amount of chromium taken up.

It has been a generally accepted belief that skins always swell in solutions of acids unless salt is present. This, however, is not true for all acids. Skins swell strongly in hydrochloric acid solution, the swelling depending on the pH of the solution, maximum swelling occurring about pH 2. In solutions of chromic acid, however, very little acid swelling occurs. The addition of

chromic acid to skins swollen with hydrochloric acid leads to a displacement of the latter by the former with a disappearance of the acid swelling. If the effect on pelt of the three strong acids, hydrochloric, sulphuric and chromic, be compared, it will be obvious that not only the pH of the acid solution but also the valency of the anion plays an important part. With increasing valency of the anion, plumping at the same pH value is less and the forces holding together the collagen-acid compound are increased. Hydrochloric acid is more readily washed out of collagen than sulphuric acid (Otto, 1933), and according to Innes, the removal of chromic acid by washing is even less complete. Chromic acid, therefore, possesses of itself some of the properties of a tan.

The increased strength of binding forces between collagen and acids that is found with increasing size of acid molecule has also been observed by Felzmann (1933).

In making up the first bath of a two-bath chrome tanning process, in order to ensure maximum absorption of the chromic acid by the pelts, hydrochloric acid and dichromate should be used in chemically equivalent proportions and no salt should be added.

## CHAPTER IV.

### THE WASHING AND NEUTRALISING OF CHROME LEATHER.

THE processes described below apply both to leather tanned by the one-bath process and also the two-bath process of chrome tanning.

Before goods are washed they are usually submitted to the process of shaving, whereby the skins are freed from any fleshy material not previously removed by fleshing. Shaving also has the effect of producing the desired "pile" in the finished leather, and to some extent of rendering the substance of the skin more even in thickness.

In the course of shaving, the roller sometimes becomes coated with a sticky grey material. This is often a danger-signal and packs of skins producing such a coating are often greasy when dried out into crust. The grey material is probably a chrome soap mixed with sulphur, hair and fleshy tissue. The cause of this phenomenon and the best method of preventing it are, however, not precisely known.

The weight of packs after shaving is invariably taken as the basis on which to calculate the various proportions of soap, oil and dye-stuff needed in subsequent operations.

#### (a) WASHING.

Washing is carried out with the object of removing most of the salts and some of the acid present in the leather. The salts are derived from residual calcium from the liming process and from the chemicals used in hypoing, and consist mostly of chlorides,

sulphates, thiosulphates, and tetrathionates of sodium and calcium. The appearance of acid in a leather originally nearly neutral (alkaline to methyl orange) is due to a slow change of the unstable leather-chromium compound whereby it gradually decomposes into a more basic stable compound and free sulphuric acid.

The salts are probably removed from the skin at about the same rate by different kinds of water, but variations in the quality of the water-supply affect the rate of the removal of the acid.

The various aspects of washing can be considered under the following headings:—

- ( $\alpha$ ) Removal of Salts.
- ( $\beta$ ) Removal of Acid.
- ( $\gamma$ ) Effect of composition of Water-supply.
- ( $\delta$ ) Temperature and Time.

( $\alpha$ ) *Removal of Salts.*

Experiment has shown that salts can be removed from goat skins of medium substance by washing for three-quarters of an hour in a good flow of running water at the ordinary temperature. It is probable that goods of a stouter substance would require a somewhat longer time than this, and that a shorter time would suffice for thinner skins. The period of washing for packs of different nature is a point which is better decided by the chemist on the spot, as the result will depend largely on the volume of water used.

This is easily accomplished by taking 2 or 3 cuttings at, say, intervals of 10—15 minutes and estimating their ash and chloride content. Well-washed goods contain practically no chloride.

( $\beta$ ) *Removal of Acid.*

It must be pointed out that the removal of acid is not so much an object of the washing process as an incidental result. Washing with a water containing much temporary hardness naturally removes part of the acid in the leather, but as a rule not enough, and the process has to be supplemented by a separate process which is discussed later under "Neutralising."

( $\gamma$ ) *Effect of Composition of Water-Supply.*

Practical experience seems to show that the best water for washing "blues" is a water containing considerable amounts of calcium bicarbonate (temporary hardness). The use of a water containing sodium bicarbonate appears to cause the leather when finished to be very loose and show a great deal of "break." The reason for this is not understood. Such waters have quite a moderate alkalinity (pH value about 8 to 8.5), which is considerably less than that of a fresh borax liquor (pH value about 9).

As the use of soft waters is always so strongly recommended for fat liquoring, some tanners have the opinion that it ought to be good for the purpose of washing. Experiments have shown that this is not the case. Trials have been made with waters (such as that condensed from a steam-engine), and with collected and stored rain water, both containing very low amounts of dissolved salts of any kind (seldom exceeding 4 degrees of temporary

hardness). It was found that such waters not only removed acid from the "blue" leather, but also dissolved out quite appreciable amounts of chromium. This does not take place with waters containing more temporary hardness, because the acid from the chrome complex is neutralised by, and there is a surplus of, calcium bicarbonate sufficient in amount to maintain the water on the alkaline side under the ordinary conditions of washing, namely, pH 7.5—8.0, at which reaction chromium cannot be removed by washing.

In the case of soft waters, sulphuric acid coming from the "blue" quickly reduces the pH of the water to 5 or less, depending on the time of action. In solutions as acid as this the chrome complex is soluble to an appreciable extent, and the leather undergoes a partial stripping, which is detrimental to its quality in the finished state.

#### (8) *Time and Temperature.*

The length of time used for washing goods in the "blue" varies from half an hour to several hours.

There is an impression in the trade that goods, especially those of light substance, can be over-washed, *i.e.*, if washed for a period much longer than that necessary to remove salts they will become empty and loose in the finished state. No work has been done on this point, and no adequate explanation is available.

As previously pointed out, salts can be largely removed by washing for three-quarters of an hour provided that there is a copious flow of water running through the drum.

In trade practice the temperature may vary from cold to 113°F. throughout the process. Satisfactory results are obtained by using cold water to commence with and water at 100°—105°F. for the last ten minutes, thus preparing the goods for neutralising, which is usually carried out at this temperature.

#### (b) NEUTRALISING.

It is well-known that, although any one tanner may use the same proportions of the same neutralising material, under the same conditions, yet at the end of the process different packs will vary in reaction to litmus paper from neutral to acid. Also, if a piece of blue litmus paper is applied to freshly-cut sections of skins, the acid zone will vary in width from a narrow strip in the middle of the section to a band almost as broad as the thickness of the section. This is possibly accounted for by variations in the constitution of the "blue" leather.

Furthermore, some tanners find that they cannot neutralise their leather by using less borax than 3 per cent. on the shaved weight. Others, however, find that their leather is neutralised if they use only 1 per cent., and further that 3 per cent. has a definite detrimental effect.

Again, leathers in the "blue" treated with even 5 to 6 per cent. borax in the cold will withstand the boiling test, but in practice this proportion of borax is said to produce most inferior leather.

Neutralisation should aim at removing excess of acid from the "blues" until a definite range of pH is reached. Theoretical considerations suggest that this range should be between pH 4.5 and

6.0, so that the full tannage of the blues is maintained. Since neutralising has to be carried out not only in relation to tanning but also to fat-liquoring, it is better for the pH value of the neutralising bath *at the end of use* to be as near as possible to 6.0.

In choosing a neutralising agent it is important to remember that:—

(a) Enough alkali must be present to combine with the free sulphuric acid in the blues.

(b) The pH should not be raised to such an extent that the stability of the chrome tanning salt is endangered.

(c) A neutralising agent should be mild in its action (of high buffer content), *i.e.*, it should be able to absorb considerable amounts of acid with only a small alteration in pH.

(d) Its solution before use should have a pH value not greater than pH 9.

(e) If a neutralising agent is used, like washing soda or soda ash, which is not mild, it should only be added to the neutralising drum in several small portions. The pH of such a solution may reach 11, but this figure is quickly lowered by the alkali being neutralised if only small amounts of alkaline solutions are added at a time. If it is added all at once it is generally considered that the external fibres become over-neutralised and plumped, and neutralisation of the internal fibres is prevented. Such external over-neutralisation would produce harsh-grained leather.

(f) The concentration of the solution as generally recommended in the case of borax should not exceed 1 lb. in 10 gallons, and the temperature should be about 100°F. It is not known why it is unsatisfactory to borax cold.

(g) The time required should be about half an hour. Less time than this does not allow equilibrium to be established so that all parts of the skin are not evenly affected. Longer than this will eventually lead to hydrolysis, with consequent formation of acid, thus defeating the object of the process.

The properties of the common alkalis can now be considered in special relation to these points.

*Caustic Soda.* This is a very strong, highly ionised and unbuffered alkali. It is never used in trade practice, and the reason is obvious from a chemical standpoint. A 1 per cent. solution has a pH of 13.3, and even such a slight excess, at the end of neutralising, as 4 parts in 10,000, would give a pH of 9. The impossibility of calculating the exact amount of caustic soda required to neutralise a pack of "blues" makes the use of this alkali, as a neutralising agent, quite impracticable.

*Sodium Carbonate* is a much milder alkali than caustic soda, but even so, 1 per cent. solutions have a pH value of about 11. There is the same difficulty in calculating the exact amount required, and an excess of alkali of 10 parts in 10,000 would leave the final liquor at pH 10.5. If sodium carbonate is used for neutralising it should only be used in  $\frac{1}{2}$  per cent. concentration and added gradually.

*Sodium Bicarbonate* is a safer neutralising agent than the carbonate. At 1 per cent. concentration it has a pH value of about 8.5. A 1 per cent. solution could, therefore, never raise the pH as high as 9, in fact even strong solutions of the bicarbonate will not reach this figure.

The disadvantage of sodium bicarbonate is that, if the solution is heated, carbon dioxide is given off and the solution then contains some carbonate. According to McCandlish, Atkin and Poulter (1934), sodium bicarbonate produces a rather less alkaline liquor than borax when the two materials are used in equivalent amounts, the use of bicarbonate involves somewhat less risk of over-neutralisation, a great economy can be effected, by substituting bicarbonate for borax, since one part of bicarbonate is equivalent to  $2\frac{1}{4}$  of borax, and the prices per ton of the two materials are of the same order, and the substitution causes no detectable difference in the quality of the finished leather.

*Borax* is a very mild and safe alkali, giving a well buffered solution with a fairly high power of combining with acids. A 1 per cent. borax solution has a pH value of 8.9. A 3 per cent. solution has a pH of 9. The use of a borax solution stronger than 3 per cent. is undesirable.

*Basic Sodium Phosphate* is a mild, well buffered alkali. In 1 per cent. concentration it gives a pH of 8.7. At  $2\frac{1}{2}$  per cent. concentration a pH value of 9 will be reached. A mixture of the acid and basic sodium phosphates should make a very safe neutralising solution.

*Sodium Thiosulphate* (hypo) has also been used as a neutralising agent for one-bath chrome blues. The strong acid from the blue is neutralised with an accompanying evolution of sulphurous acid and deposition of sulphur, the presence of which may not always be desirable. The pH of a 1 per cent. solution of sodium thiosulphate used for neutralising will be about 7 before use, but will fall during use. It should not be allowed to fall below 4.5.

A mixture of sodium thiosulphate and sodium bicarbonate or borax might be used as a neutralising agent.

It is a good plan to keep a record of the pH of the spent neutralising liquor from every pack. It can be carried out in a few seconds by the addition to the liquor of a few drops of Universal Indicator.

It should be inside the range of pH 6.5 to about 8.0. It is not meant to imply that goods from all liquors within these limits are properly neutralised, but goods from all liquors outside these limits are liable to be improperly neutralised.

No generalisations can be laid down as to what is the best proportion of alkali to use, as this will depend to a great extent on the method of washing. Variations in time of washing, the quality of the water-supply used and the amount of acid in the leather have a great effect, but possibly a more important factor still is the rate of flow of the wash-water, *i.e.*, the number of gallons per minute running into the drum.

#### (c) SWILLING OFF AFTER NEUTRALISING.

Goods which have just been neutralised should never be allowed to lie about on account of the slow hydrolysis of the chrome complex which is liable to occur at all stages—from the hypo bath until the goods have been fat-liquored.

Neutralised goods should be washed off at once for 5—10 minutes in hard water at the temperature of the subsequent dye bath, say 140°F., and are then ready for fat-liquoring and dyeing.

(d) THE CHANGES OCCURRING DURING THE NEUTRALISATION OF  
CHROME LEATHERS, AND THE SIGNIFICANCE OF THE  
APPARENT DIFFERENCE IN BASICITY, OF ONE- AND  
TWO-BATH LEATHERS.

The neutralising agents in common use in chrome tanning are salts of a strong base and a weak acid. The neutralisation of chrome blues is a process which accomplishes much more than the mere neutralisation by the strong base of the free acid taken into the tanned skins from strongly acid liquors of the chrome tanning bath. During the neutralising, chemical changes occur which involve both the basic and the acidic ions of the alkaline neutralising agent employed. While the basic ions play their usual role of neutralising the acidic ions, the neutralising agent interacts to some extent with the chrome tanning compound on the fibres, leading to an exchange of acid groups. Thus, in the neutralisation of chrome blues tanned in basic chromium sulphates, the elimination of the  $\text{SO}_4$  group from the blue is not entirely due to the neutralisation of free sulphuric acid but partly to the replacement of sulphato groups in chrome tanned collagen by the acid group of the neutralising agent (Innes, 1935). The entry of the acid group of the neutralising agent into the leather can be shown by making an estimate of the total sulphur present in a neutralised blue. Innes has obtained the following figures:—

Neutralising agent.	g. Sulphur to 52 g. chromium in neutralised blue.
Sodium bicarbonate	4.7
Sodium borate	2.0
Sodium thiosulphate	38.3
Sodium tetrathionate	51.3
Sodium phosphate	3.4
Sodium silicate	4.0
Sodium oleate	10.9

These figures show in a striking way how the total sulphur content of a leather rises if the anion of the neutralising agent contains sulphur. This sulphur is not present as sulphate but as the acid group of the neutralising agent. Thus the two-bath chrome blues have been shown by Innes to contain appreciable quantities of thiosulphate and tetrathionate.

This observation explains why the total sulphur content of a two-bath leather is always much greater than that found in a one-bath leather. Innes has shown that the deposit of colloidal sulphur in a two-bath leather is only of the order of 1 per cent. on the weight of the leather, which is not enough to account for the difference. This is due to the penetration of thiosulphate and tetrathionate groups into the chrome tanning complex. Possibly this fact alone is sufficient to account to a large extent for the characteristic difference between one- and two-bath leather. It certainly explains the very large differences in "basicity" of these two classes of leather obtained by the usual procedure of expressing all the sulphur found as  $\text{SO}_4$  and the basicity as parts of  $\text{SO}_4$  per 52 parts of Cr.

## CHAPTER V.

## WORKS CONTROL IN THE CHROME TANNERY.

CONTROL in the chrome tanning process, as practised to-day, falls into two complementary methods: (1) the control of the process and liquors and leathers by means of chemical examination, and (2) the control of the process by the foreman in charge exercising his own judgment, based on practical experience. The ideal method is a combination of chemical control and practical observation.

## CHEMICAL CONTROL.

*The analysis of chrome liquors and leathers.*

Chemical control is rendered difficult by the very many important variable factors to be considered. It will be clear from the chapter dealing with the chemistry of chrome liquors that the fact that the chemist has controlled the concentration of chromium, the pH values and the salt content of the liquors will not entirely ensure regularity in the tannage. For example, the tanning properties of sulphito chrome liquors cannot be determined from their basicity or the composition of the chromium complex.

The most important determinations to make in chemical control are the pH value, the chromium concentration, the precipitation figure and the composition and size of the chromium complex (methods for determining this are not as yet fully worked out). Observations relating to changes in pH value and the precipitation figure will often be found of great use from the standpoint of works control. Decreases in pH value in a chromium sulphate liquor, for example, are due to hydrolysis and olation. The entrance of  $\text{SO}_4$  groups into the chromium complex raises the pH value. Thus, a study of alterations in the pH value of a liquor is of considerable help in following the progress of the changes produced in the liquors by ageing and the reversal of these changes brought about by the addition of acid.

The adjustment of the tanning liquors, furthermore, is not so simple as it might appear. For example, the practical man is not in a position to take a moderately basic liquor which has undergone much olation and by the addition of a calculated amount of acid or chrome alum or chrome liquor to bring the basicity of the liquor back to the desired value rapidly. The addition will adjust the basicity of the liquor to a desired value but does not rapidly affect that of the chromium complex. Particularly is this the case for strongly olated chromium sulphate liquors. Several days must elapse after the addition of the acid in the case of liquors of moderate basicity to allow the process of olation being sufficiently reversed by the acid added.

The examination of a chrome leather can also give valuable information regarding the tanning process. It is not sufficient, however, in the examination of chrome-tanned pelt to determine the chromium content of the whole thickness. Rather must the chromium content of the various layers, and in particular of the

grain layer, be determined in a study of the most satisfactory tanning liquor and tanning conditions. An over-tannage of the grain is undesirable. Schindler and Klanfer (1929) found that the basicities over 40 per cent. cause a relative increase in the chromium content of the grain. A fresh chrome liquor of basicity 45 per cent. causes an excess of chromium to be taken up by the grain, whereas a similar liquor, allowed to age, does not deposit so much chromium in the grain. With decreasing precipitation figures the danger of over-tannage increases. Alterations in the composition of the pickle can cause big alterations in the distribution of the chromium and with an increase in the temperature of tannage, the chromium content of the grain rises more rapidly than that of the middle layer of the leather. The addition of sodium carbonate towards the end of the tannage has practically no effect on the middle layer but raises the chromium content of the grain.

Analytical methods can be divided into gravimetric and volumetric methods. From the standpoint of works control preference is usually given where practicable to volumetric methods as these are more satisfactory than gravimetric methods as being easier to carry out quickly without loss in accuracy. In order to determine chromium volumetrically the chromium should be in the hexavalent state. Trivalent chromium can be converted into hexavalent by oxidation in the presence of alkali. One-bath chrome liquors and chrome leather ashes contain trivalent chromium. This is oxidised to the hexavalent state by the use of sodium peroxide, hydrogen peroxide and sodium hydroxide, and so on in the case of chrome liquors, whereas the chrome leather ash is fused with a suitable alkaline fusion mixture to bring about the same effect. A solution which contains chromium in the hexavalent state, as for example the oxidised products just described or the first bath in the two-bath chrome tanning process, is analysed for chromium as follows: The solution is acidified with either hydrochloric acid, sulphuric acid or phosphoric acid, and excess of potassium iodide solution is added. The iodine which is liberated as a result of the interaction of the hexavalent chromium and the hydriodic acid set free from the potassium iodide is titrated with a standard solution of sodium thiosulphate, using starch paste as indicator (see below).

In order that the determinations should be reasonably accurate it is usual to adjust the concentration of chromium in the solution under analysis so that the final operation (titration in the example given above) uses reasonable quantities of reacting materials. For example, 1 c.c. of 0.1N sodium thiosulphate is equivalent to 0.00173 g. Cr. A reasonable amount of sodium thiosulphate to used in a titration would be 20—40 c.c. That is the chromium content of the liquor being titrated should be between 0.035 - 0.07 g.

In the analysis of one-bath chrome liquors and spent liquors in general difficulties can arise in the chromium determination in particular owing to the presence in the liquors of organic acids, masking materials and so on. The methods to be used for overcoming these difficulties will be described below. There does appear, however, to be one method which is applicable in the

determination of chromium when all the others are doubtful. This involves evaporating the chromium liquor to dryness, ashing the residue to remove organic matters, followed by fusion of the ash with a suitable fusion mixture and then an iodometric titration of the chromate produced in the usual way. Various methods for the analysis of chrome liquors and the leather will now be described.

## ONE-BATH CHROME LIQUORS.

### FRESH LIQUORS.

#### *Chromium (Oxidation Methods).*

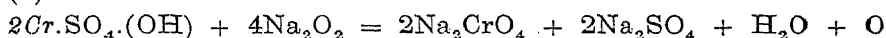
If the chromium is in the trivalent state it can be oxidised to the hexavalent state as follows:—

(a) With sodium peroxide (Alden, 1906).

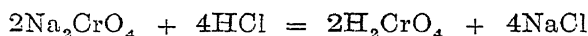
A suitable amount of the chromium solution (containing about 0.05 g. Cr) is diluted to about 50 c.c. 1—2 g. of sodium peroxide is added, a little at a time, until the colour becomes a pure yellow. The mixture is gently heated to the boil to decompose excess peroxide, care being taken to avoid loss by spray. If difficultly soluble brown chromium chromates are formed it is best to restart the determination from the beginning rather than prolong the boiling considerably in an attempt to dissolve these basic salts. Boiling is continued until effervescence ceases and boiling is steady. If the chrome liquor contains iron it will be present as a precipitate and should be filtered off, since this precipitate interferes with the later stages of the chromium determination (*i.e.*, the iodometric titration). The yellow liquor should be cooled and made acid with hydrochloric acid (free from iron and chlorine). This transforms the chromate which is present in the yellow solution into chromic acid. Excess of a potassium iodide solution is added (which must be free from iodate) and the iodine which is liberated is titrated with 0.1N sodium thiosulphate, using starch solution (a 2 per cent. solution of soluble starch) as indicator.

The various changes which occur throughout this method are given in the following equations:—

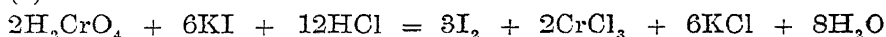
(1) Oxidation of trivalent chromium to hexavalent.



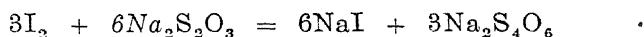
(2) Conversion of sodium chromate to chromic acid.



(3) Liberation of iodine.



(4) Iodometric titration.



That is  $6Na_2S_2O_3 \equiv 2Cr$

or  $60000 \text{ c.c. } 0.1N.Na_2S_2O_3 \equiv 2Cr \equiv 104 \text{ g. Cr}$

and  $1 \text{ c.c. } ,, ,, \equiv 0.00173 \text{ g. Cr}$

or  $\equiv 0.00253 \text{ g. } Cr_2O_3.$

(b) With hydrogen peroxide (Proposed Official Method of the I.S.L.T.C., *J.I.S.L.T.C.*, 1929, 111).

“ The chromium solution (containing about 0.035—0.070 g. Cr) is diluted to about 150 c.c. Normal sodium hydroxide is added sufficient to give an excess of 10 c.c. 10 c.c. of hydrogen peroxide (10 volumes) are added, and the solution raised to the boil, care being taken to prevent loss by frothing. The boiling may be continued with a small piece of clean iron introduced until it “ rattles ” against the glass (indication of complete decomposition of excess peroxide), less than five minutes being usually required for this. The piece of iron is removed, any suspended ferric hydroxide (due to small amounts of iron originally present in the sample) is filtered off, and the cooled alkaline solution treated with concentrated hydrochloric acid sufficient to produce an excess of 5 c.c. 15 c.c. of 20 per cent. potassium iodide solution are added, and the iodine liberated titrated with 0.1N sodium thiosulphate. (1 c.c. of 0.1N sodium thiosulphate is equivalent to 0.00253 g. of  $\text{Cr}_2\text{O}_3$ ). ”

(c) With potassium permanganate. (Proposed Alternative Official Method of the I.S.L.T.C., *J.I.S.L.T.C.*, 1929, 111).

“ An amount of chrome liquor containing 0.17—0.35 g. of Cr is oxidised with peroxide as above, cooled and diluted to about 400 c.c. in a 500 c.c. graduated flask. 5 c.c. of cold saturated potassium permanganate solution is added. The mixed solution is diluted to the 500 c.c. mark, well shaken, filtered, and 100 c.c. of the filtrate treated with excess of hydrochloric acid and potassium iodide solution as above. (Reference: Wagner, 1924). ”

According to Schorlemmer (1917), the chromium solution is brought to the boil after being made decidedly alkaline with sodium hydroxide, a very slight excess of potassium permanganate solution added and the excess removed by adding alcohol a drop at a time. The solution is filtered and the chromate determined iodometrically.

(d) With Bromine Water. (Feigl, Klanfer & Weidenfeld, 1929).

25 c.c. of the chromium solution is mixed with 10 c.c. of 20 per cent. sodium hydroxide and then 25—30 c.c. of saturated bromine water is added. The mixture is boiled for 5 minutes until a pure yellow. Excess hypobromite can be removed by the addition of potassium thiocyanate.

Many workers have pointed out the difficulty of oxidising chromium in the presence of organic matter, as, for example, in the case of used liquors or a glucose liquor containing excess of glucose, and so on. One method of overcoming this difficulty is to precipitate the chromium as hydroxide (with ammonia) filtering off the precipitate, dissolving in dilute hydrochloric acid and proceeding as usual. This is, however, not satisfactory where the chromium compounds are masked, since owing to the presence of organic groups in the chromium complex the precipitation of the chromium by ammonia will not be complete. In such cases the chrome liquor should be evaporated to dryness, ignited to remove organic matter and then the chromium determined in the manner described later for the ash of a chrome leather.

Other methods for dealing with the presence of iron and organic matters in chrome liquors are given later under the analysis of "Used Liquors" for chromium.

#### *Chromium (Conductometric Method).*

A method which does not involve oxidation of the trivalent chromium is that described by Theis and Serfass (1934), in which the chromium is determined by conductometric titration [except in the case of chromium complexes containing sulphate (sulphato) groups]. 30 c.c. of 0.1N HCl are added to 50 c.c. of chrome liquor (0.1 per cent. Cr) and the resulting solution boiled not less than 3 hours. After cooling, this solution is then titrated conductometrically using 0.1N NaOH. Two "kink" points are obtained in the curve if the conductivity is plotted against the addition of alkali. The difference between these "kink" points gives the c.c. of 0.1N chromium present in the sample.

#### *Percentage Basicity.*

(Expressed according to the Schorlemmer Method (1920); accepted as official by the I.S.L.T.C., *J.I.S.L.T.C.*, 1924, 65).

Schorlemmer's method of defining the percentage basicity of a chrome liquor is as follows:—Percentage basicity is the chromium combined with hydroxyl expressed as a percentage of the total chromium.

The chrome tanning salt present in a chrome liquor contains acid groups and hydroxyl groups associated with the chromium. The acid groups can be displaced by the addition of sodium hydroxide giving chromium hydroxide. In chromium hydroxide the chromium atom is associated with 3 hydroxyl groups and the percentage basicity of this compound is 100. The percentage basicity of a chromium compound can, therefore, be regarded as the percentage amount of hydroxyl it contains per atom of chromium compared with the amount of hydroxyl in chromium hydroxide.

For example, a chromium compound containing one hydroxyl group per atom of chromium has a percentage basicity of 33.3 per cent. and contains one third or 33.3 per cent. of the amount of hydroxyl (3 groups) in chromium hydroxide. Similarly, a percentage basicity of 66.7 per cent. corresponds with  $\frac{2}{3}$  of the hydroxyl groups in chromium hydroxide, namely,  $\frac{2}{3}$  of 3, which is 2. The following are examples of the compounds just described:—

$\text{Cr}(\text{OH})\text{SO}_4$ ; 33.3 per cent. basic chromium sulphate.

$\text{Cr}(\text{OH})_2\text{Cl}$ ; 66.7 per cent. basic chromium chloride.

In the analytical determination of percentage basicity, a definite amount of the chrome liquor is titrated with 0.1N sodium hydroxide to find the amount of sodium hydroxide which is required to convert the whole of the chromium in that amount of liquor into chromium hydroxide. If this is denoted by "b" and "a" denotes the c.c. 0.1N sodium thiosulphate which is equivalent to the amount of chromium in the same volume of chrome liquor, then (a - b) denotes the amount of hydroxyl which the chromium compound contains and the percentage

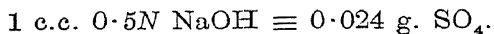
basicity is  $100(a - b)/a$ . Furthermore, "b" is a measure of the sum of the acid combined with chromium and any free acid which the chrome liquor contains. It can be expressed as  $\text{SO}_4$  or Cl according as to whether the chrome liquor is a sulphate liquor or a chloride liquor. "b" can be used as a practical guide if it is desired to adjust the basicity of the chrome liquor to which it applies.

The titration with sodium hydroxide is carried out, according to the Official Method of the I.S.L.T.C., *J.I.S.L.T.C.*, 1924, 504, as follows:—

"Commercial chrome liquors are sold in concentrated form and are very viscous, so that a suitable quantity must be weighed out and diluted to a known volume with distilled water.

"A measured quantity of the diluted solution (containing 0.2 to 0.3 g. of chromium) is diluted to about 400 c.c. in a porcelain basin, 3 to 4 c.c. of 1 per cent. phenol phthalein added and titrated in the cold with 0.1N NaOH until a pink colour develops, stirring constantly. The contents of the basin are then boiled and the titration continued. When nearing the end point the bunsen should be removed and the titration completed.

"The end-point is seen by a greyish violet tint of the well stirred liquid, or by a distinct pink colour seen on the side of the basin, after allowing the precipitate to settle."



The method given by Stiasny (*Gerbereichemie*, p. 411) is as follows:—400 c.c. of distilled water are placed in a white porcelain dish, 3—4 c.c. 1 per cent. phenol phthalein added and titrated with 0.1N sodium hydroxide at the boiling point until a faint pink. 25 c.c. of the chrome liquor (0.1 per cent. Cr) which has previously been titrated in the cold with 0.1N NaOH against phenol phthalein to a faint pink, is then added. The titration with 0.1N NaOH is continued slowly at the boiling point with good stirring. It is necessary to keep the solution boiling. The addition of 50 g. absolutely pure sodium chloride to prevent the precipitation of basic chromium sulphates during the titration instead of chromium hydroxide is not absolutely necessary.

#### Observations.

The titration methods described above are affected by the following factors:—

- (1) The presence of iron and aluminium in the chrome liquor.
- (2) The presence of masking substances which prevent the complete precipitation of the chromium.
- (3) The presence of volatile acids in the chrome liquor, such as formic, acetic, sulphurous, carbonic (in liquors to which sodium carbonate or bicarbonate has been added at any stage). These acids are displaced from their salts with alkali metals by sulphuric acid set free from the chromium salt in the liquor on hydrolysis. Volatile acids can be determined if the titration is carried out in an apparatus fitted with a reflux condenser or they can be driven off by distillation or displaced by boiling with sulphuric acid and titrated separately.
- (4) The presence of ammonium salts which interact with the sodium hydroxide.

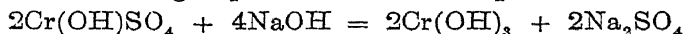
It has been suggested that the difficulty just described in the case of volatile acids and carbonate salts (which decompose on boiling) could be overcome by starting the titration in the cold and not heating until the solution being titrated has turned red, then completing as usual. This procedure, however, does not eliminate the difficulty mentioned above that the salts of the volatile acids would be decomposed during the heating of the solution by the sulphuric acid set free by hydrolysis from the chromium compound.

For anionic or masked chromium liquors, Burton, Glover and Wood (1922), proposed the following method which involves an oxidation process:—

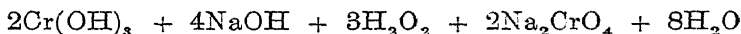
25 c.c.  $\text{H}_2\text{O}_2$  (20 per cent. by volume) are added to 50 c.c. of chrome liquor (0.5 per cent. Cr) followed by 30 c.c.  $\text{N.NaOH}$ . The mixture is diluted with 50 c.c. water, boiled 30 minutes avoiding loss by spray, acidified with 25 c.c.  $\text{N.H}_2\text{SO}_4$ , boiled for a short time and, after dilution with water, the excess acid is titrated with sodium hydroxide using phenol phthalein as indicator. For the determination of chromium this solution is acidified with 10 c.c. concentrated  $\text{HCl}$ , diluted to 500 c.c. and 50 c.c. titrated iodometrically with thiosulphate.

The sodium hydroxide used in the above method reacts as follows:—

(1) With the acid groups in the chrome liquor.



(2) To oxidise the chromium.



The total alkali used up can be corrected for the amount used in oxidising the chromium ( $2\text{Cr} \equiv 4\text{NaOH}$ ), thus giving the amount used in reacting with the acid groups. If the amount of 0.1N thiosulphate used for the 10-fold diluted liquor is " $a$ ," then since  $2\text{Cr} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$ , the amount of  $\text{N.NaOH}$  used in the chromate formation (equation 2) is  $2/3.a$ .

The amount of alkali used is

$$\begin{aligned} &= 30 \text{ c.c. N.NaOH} - 25 \text{ c.c. N.H}_2\text{SO}_4 + b \text{ c.c. N.NaOH} \\ &= 5 + b \text{ c.c. N.NaOH} \end{aligned}$$

then the  $\text{NaOH}$  used for reacting with the acid groups

$$= 5 + b - \frac{2a}{3} \text{ c.c. N NaOH}$$

$$\text{and the percentage basicity} = \frac{a - (5 + b - \frac{2a}{3})}{a} \times 100$$

$$\text{or} \quad \frac{\frac{5}{3}a - b - 5}{a} \times 100.$$

This method fails if organic substances are present in the chrome liquor which combine with alkali on boiling with sodium hydroxide and  $\text{H}_2\text{O}_2$ , for example, partial oxidation products of carbohydrates, glucose-reduced liquors which contain dextrin, with carbonate chromium derivatives, since the sodium carbonate formed is decomposed by the boiling with sulphuric acid, and if thiosulphates and polythionates are present, as in thiosulphate reduced liquors, which consume alkali in their oxidation with  $\text{H}_2\text{O}_2$ .

Theis and Serfass (1934) describe a conductometric method of determining basicity which they claim is not affected by the concentration of the chromium in the sample, whereas the hot titration method using phenolphthalein and sodium hydroxide is. The chrome liquor is diluted to approximately 0.1 per cent. Cr and titrated (50 c.c.) with 0.1N NaOH by the conductance method to a "kink" point, i.e., a kink in the curve plotted from conductivity against added alkali. The "kink" point corresponds to the end point in the ordinary hot titration.

*The average percentage basicity of the chromium salt in the liquor.*

The percentage basicity of a chrome liquor does not necessarily give the percentage basicity of the chromium salt in the liquor, since the liquor may contain free acid formed by hydrolysis of the chromium salt. Thus the percentage basicity of the chromium salt in the liquor will be greater than the percentage basicity of the liquor by the amount of free or hydrolytic acid in the liquor.

The free acid in a chrome liquor can be determined by titration to a definite pH value with a suitable indicator using a comparator. The method suggested is a modification of that described later under the determination of the degree of olation of a chrome liquor. According to Stiasny (*Gerbereichemisches Taschenbuch*, 1932, p. 155) the determination is only of practical interest if the chrome liquor has a pH value less than 2.8 for it is only then that the amount of alkali used up by the free acid is appreciable. This occurs with chrome liquors which are completely olated and which contain considerable amounts of free acid in addition to olated basic chromium complexes.

Theis and Serfass (1934) determined the free acid (due to hydrolysis) in a chrome liquor conductometrically. 50 c.c. of chrome liquor (0.1 per cent. Cr) is diluted with 30 c.c. water and titrated immediately by the conductance method using 0.1N NaOH.

*Precipitation Figure and Basicity.*

The precipitation figure, which can be regarded as a measure of the astringency of a chrome liquor, can be defined as the amount of alkali which can be added to a chrome liquor to just bring about a cloudiness. According to Stiasny (*Gerbereichemisches Taschenbuch*, 1932, p. 158) it can be determined as follows:—

25 c.c. of clear chrome liquor (0.1 per cent. Cr approximately) are titrated slowly in a small glass vessel with 0.1N NaOH until slight turbidity occurs. The result expressed as c.c. 0.1N NaOH per 25 mg. Cr is the precipitation figure.

The precipitation basicity (the basicity of the chrome liquor at the precipitation point) is calculated from the following expression (Fritsch, 1925).

If for the same amount of chrome liquor,

$a$  = c.c. 0.1N thiosulphate used in the Cr determination,

$b$  = c.c. 0.1N NaOH used in the basicity determination, and

$c$  = c.c. 0.1N NaOH used in the precipitation point determination,

then the precipitation basicity =  $(a - b + c) \times 100/a$ .

It is sometimes found to be of more practical value to carry out the determination of the precipitation figure by using in the titration that alkali which is used in the tanning process for adjusting basicity or for neutralising a chrome leather. The method of determination remains unchanged but the results are reported in terms of the alkali used. The method described by McCandlish (1917) takes this into account. In this method "the chrome liquor is mixed with kaolin, filtered and 10 c.c. of the perfectly clear filtrate is measured into a beaker of about 50 c.c. capacity. A 0.1N or 0.05N solution of alkali such as is ordinarily used for neutralising the liquor in the process (borax, sodium bicarbonate, sodium carbonate, etc.) is slowly run into the beaker from a burette. The precipitate which at first forms is re-dissolved as the beaker is agitated, but finally a point is reached where a permanent turbidity is produced in the chrome solution. For the sake of convenience this is called the precipitation point. It is a danger point which may be easily passed when neutralisation of the liquor is not properly controlled."

For practical purposes it is sometimes found useful to express the result as lbs. of the alkali used to produce a turbidity in 1 gallon of the chrome liquor.

According to Elöd and Cantor (1934), there is a parallel relation between the precipitation figure of a chrome tanning liquor and the uptake of chromium by the pelt.

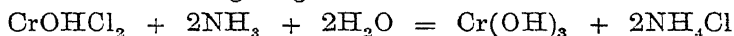
*pH Value.* (Proposed Official Method of the I.S.L.T.C., J.I.S.L.T.C., 1929, 112).

"The determination of the hydrogen ion concentration of a chrome liquor presents no special difficulty. The colour usually prevents the satisfactory use of an indicator. Hence an electro-metric method must be employed using either the hydrogen or the quinhydrone electrode."

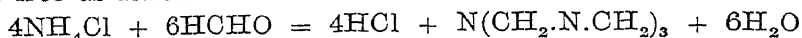
*Acid groups associated with chromium.*

The determination of the acid groups in chrome liquors and leather has attracted considerable attention in recent years and in particular use has been made of modifications of the formal titration method described by M. Bateson (1911). Bateson's method was used for the determination of the acidity of one-bath chrome liquors and was based upon the following reactions.

(1) On the addition of ammonia to a chrome liquor the chromium is precipitated as hydroxide and the acid groups link up with the ammonia giving ammonium salts.



(2) If formaldehyde is thereupon added, these acid groups are set free as follows:—



(3) The acid can be titrated and the amount of acid groups in the original liquor calculated from the titration.

1 c.c. 0.5N NaOH  $\equiv$  0.024 g.  $\text{SO}_4$  or 0.017 g. Cl.

50 c.c. of chrome liquor (0.5 — 1 per cent.  $\text{Cr}_2\text{O}_3$ ) are placed in a 100 c.c. graduated flask together with phenol phthalein as indicator. Ammonia is added until the phenol phthalein is reddened, the mixture made up to 100 c.c., well shaken and filtered. 10 c.c. of neutral formaldehyde (40 per cent.) is added to 50 c.c. of the filtrate and the mixture titrated with 0.5N NaOH to a pink colour. The method fails if amino acids or ammonium salts are present in the chrome liquor.

Stiasny and co-workers (*Coll.*, 1929, 567; *Gerbereichemisches Taschenbuch*, 1932, p. 153) modified this method and formulated what they term the "Formol-Barium Chloride method." In this method the chrome liquor is precipitated by ammonia but at the same time barium chloride is also added. Any  $\text{CO}_2$  or  $\text{SO}_4$  groups which are present in the chrome liquor associated with chromium are precipitated as barium carbonate or sulphate respectively, giving an equivalent of ammonium salt which can be determined by the addition of formaldehyde as described above. the method is as follows:—

50 c.c. of the chrome liquor containing about 1 per cent. of chromium is mixed with 25 c.c. of ammonia (approximately normal), 12 c.c. of ammonium chloride solution (approximately molar) and 6.8 g. barium chloride dissolved in a little water. The mixture is heated in a flask fitted with a reflux condenser, the exit of which is protected against the inlet of  $\text{CO}_2$  by means of a soda lime tube. The mixture is then allowed to stand, preferably overnight, and rapidly filtered, the filtrate being collected in 30 c.c. of 0.2N HCl in a litre graduated flask. The filter paper and precipitate are well washed and the washings and filtrate made up to 1 litre. 100 c.c. of this is then taken for the formol titration. In order to avoid the use of neutralised formaldehyde a blank test is run using the above amounts of ammonium chloride and HCl making the blank up to 1 litre with distilled water. For the formol titration 5 c.c. of approximately 40 per cent. formaldehyde is added and the solutions titrated with 0.2N NaOH to a deep red, then to pale red with 0.2N HCl and finally to red with 0.2N NaOH (2 or 3 drops). From the difference in the titrations for the experimental solution and the blank the amount of acid groups in the original chrome liquor can be calculated. The method fails where chromium complexes are present which are stable to the action of alkali, where the chrome liquor contains ammonium salts which are determined as acid and  $\text{SO}_2$  groups which are only determined to 50 per cent. due to the combination of the  $\text{SO}_2$  with formaldehyde. Later in this chapter information is given as to the determination of the various individual acid groups in chrome leather and it is suggested that the methods described there can be applied to chrome liquors after their treatment as described above.

*Volatile Acids.*

As suggested earlier in this chapter, volatile acids such as formic, acetic and carbonic can be displaced from a chrome liquor by distillation with sulphuric acid. The acids are collected and determined in the usual way. In the case of carbonate salts the  $\text{CO}_2$  is collected in a suitable absorption apparatus.

*Degree of Olation.*

The presence of an OH group appears to be the first essential in a chrome tanning salt which must also be soluble in water or the chromium compound, if it contains no OH group, must when dissolved in water, produce a salt containing an OH group. As will be shown in Chapter VI, the OH groups in a chrome liquor can occur in two forms, one in which it is titratable with acid and a second or "olated" form in which the OH group or "Ol" group, as it is called, shows considerable stability towards acids. This difference between olated and ordinary OH groups is the basis of a method described by Stiasny and Königfeld (1932) for the determination of the degree of olation of chrome liquors.

A suitable amount of 0.1N HCl is added to the chrome liquor and the excess acid titrated immediately. From the amount of acid used up the amount of the titratable OH groups can be calculated. In a further test, the chromium liquor is heated with a suitable amount of 0.1N HCl, cooled, and the excess of acid titrated. In this test the acid used up corresponds to the sum of the olated and of the titratable OH groups.

If  $x$  = c.c. 0.1N HCl added to 50 c.c. of chrome liquor (0.1 per cent. Cr),

$y$  = c.c. 0.1N NaOH used in back titration of the HCl used in the cold,

and  $z$  = c.c. 0.1N NaOH used in back titration of the HCl used in the hot,

then  $x - y$  = acid used up by the titratable OH groups,

and  $x - z$  = acid used up by the total OH groups

$(x - z) - (x - y) = y - z$  = acid used up by the olated OH groups.

Therefore the degree of olation (as a percentage) =  $\frac{y - z}{x - z} \times \frac{100}{1}$ .

In the back titration of the excess acid it is necessary to choose an indicator which in a mixture of a normal chromium salt (0 per cent. basicity) and hydrochloric acid allows the latter to be determined and avoids titration of the chromium salt. This is attained if the pH value at the end of the titration is 2.8, which is the pH of a chromium chloride solution (0 per cent. basicity) containing 1 g. Cr. A suitable indicator for this purpose is benzene-aniline-azo-benzene-sulphonic acid. This indicator is sold in the form of its potassium salt by Merck (*p*-benzol-sulphonsäure-azo-benzyl-aniline) or as the half-titrated sodium salt by the British Drug Houses, Ltd. 10 c.c. of a 0.01 per cent. aqueous solution of this indicator is added to the acidified chromium salt solution and

the solution is titrated, using a comparator with 0.1N sodium hydroxide to colour equality with a buffer solution of pH = 2.8 (0.14N acetic acid solution).

For basic chromium chloride solutions, the following quantities have been found satisfactory:—25 c.c. 0.1N HCl to 50 c.c. of a chrome liquor containing 0.1 per cent. Cr.

For chromium sulphate solutions, however, matters are rather different. An addition of 25 c.c. 0.1N HCl to 50 c.c. of a chromium sulphate liquor containing 0.1 per cent. Cr is not sufficient to free the olated OH groups on heating. All basic chromium salts tend to olate on heating, and in the case of the basic chromium sulphates this tendency is so great that a normal chromium sulphate solution requires the addition of 75 c.c. HCl so that on boiling, hydrolysis and subsequent olation of the basic chromium salts is prevented. If less than 75 c.c. 0.1N HCl are added to a chromium sulphate solution of 0 per cent. basicity, then after 60 minutes boiling, titration to pH 2.8 reveals an increase in the amount of free acid. This is of great importance as it will occur with all chromium salts which show a strong tendency to hydrolysis and olation. In such cases it has been found simpler not to determine the total OH groups by boiling after addition of acid and so on, but to calculate this value from the basicity of the solution.

The degree of olation can also be expressed in another way, namely:—

$$\text{Degree of olation} = \frac{a - b - c}{a - b} \times \frac{100}{1}$$

in which  $a$  = c.c. 0.1N thiosulphate for Cr determination,

$b$  = c.c. 0.1N NaOH for basicity determination,

$c$  = c.c. 0.1N HCl for reaction with the titratable OH groups.

the same volume of liquor being used throughout.

The titration of the acidified chrome liquor to a pH of 2.8 is carried out in a comparator as follows:—

No. 1 tube of the comparator contains 7.5 c.c. of the comparison solution at pH 2.8 (0.14N acetic acid) + 1 c.c. of indicator solution.

Tube No. 2 contains 5 c.c. of the chrome liquor (0.1 per cent. Cr) and 5 c.c. water.

Tube No. 3 contains distilled water.

Tube No. 4 contains the titration liquor. The titration is carried out in a beaker. 50 c.c. of the chrome liquor are treated with 25 c.c. 0.1N HCl and 10 c.c. of indicator solution and then titrated with 0.1N NaOH. Towards the end point of the titration 10 c.c. of the titration liquor is placed in the tube No. 4 for matching. This is returned to the titration beaker, the titration carried further and the testing and further titration repeated until nearly complete. The contents of tube No. 1 are next adjusted for concentration of indicator by the addition of an amount of the comparison solution equal to one tenth of the volume of 0.1N NaOH used in the titration. The titration is continued further until a matched endpoint is attained. Tube No. 1 must be made up fresh

for each test, since the colour gradually fades. The results enable "c" (see above) to be calculated. The determinations of "a" and "b" respectively have been described earlier, "a" being the determination of chromium and "b" the basicity of the chrome liquor, both "a" and "b" being expressed as c.c. 0.1N solutions.

The method is not directly applicable to organic chrome salts or in the presence of buffer substances. Furthermore, it gives no information as to the molecular weight of the chromium salts in the liquor. It thus requires supplementing by a direct determination of the molecular size of the chromium complexes (see Chapter VI). Theis and Serfass (1934) have attempted the determination of the degree of olation of commercial types of chrome liquors. They analysed several chrome liquors by the above method of Stiasny and Königfeld, and encountered considerable difficulty in obtaining an end point at pH 2.8. Titration was thereupon carried out to pH 2.8 by the use of the glass electrode and it was found that when the amount of 0.1N HCl added varied from 25 c.c. the amount of acid penetrating or neutralising the OH groups varied considerably when determined through titration to pH 2.8. It was later found that conductometric methods could be used to determine the free acid penetrating into the nucleus of the chromium complex. Instead of titrating to a set end point of pH 2.8, the solution was titrated conductometrically to a "kink" point. The possibility of excessive penetration of acid into the complex, thereby displacing aquo groups, it is suggested, could be eliminated by lowering the concentration of the acid added to a dilute solution of the chrome liquor, enabling olation to be accurately determined conductometrically. The amount of titratable OH groups in the chrome liquor are determined conductometrically as follows:—

The liquor is diluted to approximately 0.1 per cent. Cr. To 50 c.c. add 30 c.c. 0.1N HCl and titrate immediately with 0.1N NaOH by the conductance method. The degree of olation is then calculated from the usual formula.

Theis and Serfass found that the results for the degree of olation by the conductometric method were decidedly different in all cases to those obtained by Stiasny's method.

Theis and Serfass also used conductometric methods for the determination of chromium, per cent. basicity, free acid (by hydrolysis) and so on. Their methods are given earlier under these headings.

#### *Molecular Weight.*

The molecular weight of the chromium salt in a chrome liquor has been determined from the diffusion coefficient (see Chapter VI). The average molecular weight of the dissolved substances in a chrome liquor can be determined by means of the Freezing Point Method (Depression of the Freezing Point) provided the concentration of dissolved salts is not too low.

#### USED LIQUORS.

##### *Chromium.*

The volume taken for analysis will necessarily be greater than for fresh liquors, since the liquors are much weaker.

Used liquors are more troublesome than fresh liquors for a variety of reasons. They frequently contain considerable amounts of calcium (from the goods being tanned). This is converted into calcium peroxide, which is precipitated during the boiling of a chrome liquor with peroxide and can be removed by filtration before the chrome liquor is acidified. (Proposed Official Method, *J.I.S.L.T.C.*, 1929, 112.) Unless this is done the iodometric result will be too high owing to the  $\text{CaO}_2$  liberating iodine in the presence of  $\text{HCl}$ . The filtered solution is then treated with acid and potassium iodide and titrated with thiosulphate in the usual way.

A further method of dealing with the presence of calcium is that of Kubelka and Wagner (1926). The chrome liquor is treated with potassium hydroxide until the precipitate formed dissolves, then a further 1 c.c. 25 per cent.  $\text{KOH}$  is added, followed by 10 c.c.  $\text{H}_2\text{O}_2$  (3 per cent.). The mixture is warmed on a water bath and then heated freely for 10 minutes. The yellow solution is treated with  $\text{N.KMnO}_4$ , a drop at a time, as long as a brown precipitate is formed. Excess of permanganate (denoted by a pink colour) must be avoided. This can be removed by the addition of diluted alcohol, a drop at a time. The mixture is shaken until gas evolution ceases, after which, chromium is determined by iodometric titration.

Used liquors can also contain organic materials which stabilise  $\text{H}_2\text{O}_2$  and on acidification have a reducing action on chromic acid. An alternative method to the  $\text{H}_2\text{O}_2$  oxidation is the use of bromine water (see below) or potassium permanganate as oxidising agent. Organic materials such as excess glucose will reduce the chromic acid. As suggested previously, in exceptional cases, ignition after evaporation is a suitable method of getting rid of organic substances, the ash being then oxidised in the manner described under chrome leather analysis.

If iron is present then its effect can be counteracted if the oxidised solution (with peroxide or hypobromite) is acidified with 3N phosphoric acid until the precipitate formed is re-dissolved (Barnebey, 1917). Then 15 per cent. sodium iodide solution is added and the iodine set free titrated as usual with thiosulphate. Another method is to add ammonium fluoride to the oxidised solution after acidification with  $\text{HCl}$  (Little and Costa, 1921) until the solution no longer gives an iron reaction with potassium ferrocyanide. A further 1 g. ammonium fluoride is added and the chromium determined iodometrically.

The bromine water method of oxidation referred to above is carried out as follows (Feigl, Klanfer and Weidenfeld, 1929):—

Excess of  $\text{NaOH}$  is added to the chrome liquor (about 10 c.c. 20 per cent.  $\text{NaOH}$ ) and 25–30 c.c. saturated bromine water. The mixture is boiled for 5 minutes. The excess of hypobromite can be removed by adding not more than 10 c.c. of a 2 per cent. solution of potassium thiocyanate and boiling not longer than  $\frac{1}{2}$ –1 minute. The cooled solution is titrated with thiosulphate after the addition of  $\text{KI}$  and  $\text{H}_2\text{SO}_4$ . If iron is present then the solution should be acidified with phosphoric acid, as described above, instead of sulphuric acid. If proteins are present in the chrome liquor then they separate as a white precipitate in the oxidation process and do not disturb the iodometric titration.

For chrome liquors which contain thiosulphate the method of treatment is to oxidise the acid solution with bromine water, boil off excess, then render alkaline and proceed as usual.

#### *pH Value.*

The pH value of used chrome liquors can be determined electrometrically. Where the used liquors are sufficiently light in colour colorimetric methods will be found quite suitable.

#### *Percentage Basicity.*

This can be determined as described earlier under fresh liquors.

### TWO-BATH CHROME TANNING LIQUORS.

#### FIRST BATH.

##### FRESH LIQUORS.

The analysis of the first bath of the two-bath process of chrome tanning involves two determinations: (a) the amount of hexavalent chromium (as c.c. 0.1N thiosulphate) and (b) the amount of 0.1N NaOH (c.c.) necessary to redden phenol phthalein when added as an indicator to the chrome liquor. The relation between "a" and "b" for the same volume of chrome liquor is interpreted as follows:—

TABLE II.

Value of $\frac{a \text{ (c.c. 0.1 N. Na}_2\text{S}_2\text{O}_3\text{)}}{b \text{ (c.c. 0.1 N. NaOH)}}$	The chrome solution contains:—	Calculation of the results.
$\infty$ ( $b = 0$ )	Monochromates only	$a \times 0.0065 \text{ g. K}_2\text{CrO}_4$
$> 3$	Mono and di- chromates	$(a - 3b) \times 0.0065 \text{ g. K}_2\text{CrO}_4$ $b \times 0.0147 \text{ g. K}_2\text{Cr}_2\text{O}_7$
3	Dichromates only	$a \times 0.0049 \text{ g. K}_2\text{Cr}_2\text{O}_7$
$< 3 > 1.5$	Dichromates and chromic acid	$(2a - 3b) \times 0.0049 \text{ g. K}_2\text{Cr}_2\text{O}_7$ $(3b - a) \times 0.0033 \text{ g. CrO}_3$
1.5	Chromic acid only	$a \times 0.0033 \text{ g. CrO}_3$
$< 1.5$	Chromic acid and hydrochloric acid	$a \times 0.0033 \text{ g. CrO}_3$ $(b - \frac{2a}{3}) \times 0.00365 \text{ g. HCl}$
0 ( $a = 0$ )	Hydrochloric acid only	$b \times 0.00365 \text{ g. HCl}$

##### USED LIQUORS.

Spent liquors from the first bath in the two-bath chrome tanning process contain both tri- and hexa-valent chromium. The latter can be determined directly whilst the total chromium can be determined after oxidation by the methods described for spent one-bath liquors. The difference between the two chromium determinations gives the amount of trivalent chromium in the liquor.

#### SECOND BATH.

##### USED LIQUORS.

##### *Chromium.*

Spent liquors from the second bath of the two-bath chrome tanning process can be analysed for chromium as described for

spent one-bath liquors. In the case of used hypo liquors, however, the boiling with sodium peroxide will convert tetra-thionates which are present in the used liquor into thiosulphate. In such cases it will probably be found preferable to precipitate the chromium as hydroxide, filter and re-dissolve the chromium hydroxide in  $\text{HCl}$ , render alkaline, oxidise with  $\text{H}_2\text{O}_2$  and then proceed as usual.

#### *Thiosulphate.*

Thiosulphate in both spent and fresh liquors can be determined in the ordinary way. There is always the possibility that the spent liquor may contain dissolved sulphur dioxide if the pH value is too low.

#### *Sulphur Dioxide.*

The excess of  $\text{SO}_2$  produced by using an excess of mineral acid in the second bath can be determined by observing the amount of  $0.1\text{N K}_2\text{Cr}_2\text{O}_7$  necessary to produce a yellowish green colour with 25 c.c. of the filtered liquor (Innes, 1925).

#### *pH Value.*

The pH value of the used liquor is of importance and can be determined colorimetrically or electrometrically by the use of the glass electrode.

### CHROME LEATHER.

#### *Grease.*

This can be determined by Soxhlet extraction of 15 to 20 g. of the finely divided leather with petroleum ether (light petroleum). It has been shown by Innes (1919) and confirmed (Sub-Committee Report, *J.S.L.T.C.*, 1920, 295) "that under the conditions of a Soxhlet extraction, petroleum ether extracts as much sulphur from chrome leather as carbon disulphide." The extraction is continued for 3 to 4 hours and the grease residue left after evaporation of the solvent on a water bath dried at  $100$  to  $105^\circ\text{C}$ . Procter (*Leather Chemists' Pocket Book*, p. 195) dries the chrome leather for 3 to 4 hours at  $100$  to  $105^\circ\text{C}$ . to remove most of the moisture prior to the Soxhlet extraction. The International Commission on the analysis of chrome liquors and leathers also proposed that the leather be dried before petroleum ether extraction (*J.I.S.L.T.C.*, 1925, 508).

#### *Moisture.*

5 g. of the finely cut up leather is dried at  $100$ — $105^\circ\text{C}$ . to constant weight, the loss during the drying process being taken as moisture (*Leather Chemists' Pocket Book*, p. 194). In the Official Method of the I.S.L.T.C. (*J.S.L.T.C.*, 1924, 61), 5 g. of the cut up sample (pieces not greater than  $0.5$  cm. square) are weighed in a flat-bottomed dish and heated at  $105^\circ\text{C}$ . for 2 hours, rapidly transferred to a dried weighing bottle cooled in a desiccator and weighed.

### *Ash.*

3—5 g. of the finely cut up leather is ashed in the usual way until free from carbon in a platinum crucible or dish. The ash is examined further for chromium content as described below. In the Official Method of the I.S.L.T.C. (*J.S.L.T.C.*, 1924, 62), the leather is added gradually to the dish (preferably platinum) heated to a dull red, the temperature being raised to a bright red heat when all volatile matter has been driven off.

### *Hide Substance.*

This is determined by Kjeldahl's method. Frey, Jenkins and Joslin (1928) find no need for degreasing the leather before Kjeldahling, whereas Burton (1928) finds that lower nitrogen figures are obtained if the determination is carried out on the degreased sample.

### *Matters Soluble in Water.*

These can be determined by extraction of the degreased leather in a Procter extractor, using water at a suitable temperature. In the *Leather Chemists' Pocket Book* "nearly boiling water" is used in the extraction. It is recommended (Innes, 1931) that the finely divided sample of leather should be given a preliminary soaking in hot water and allowed to stand for 24 hours at laboratory temperature.

### *pH Value of Aqueous Extract.*

It has been suggested (Ingle, 1928) that useful information might be forthcoming from a comparison of the chromium content of a leather with the pH of an extract prepared by boiling the leather with a known amount of water. Mudd and Pebody (1929) investigated this and boiled chrome leather with water, using a reflux condenser. The pH value of the extract varied with the ionogenic sulphate in the leather and the method could be used as a control on the neutralising process. The method of extraction was as follows:—15 g. of finely divided leather was degreased in a Soxhlet, freed from the degreasing solvent (petroleum ether) "transferred to a conical flask with 150 c.c. distilled water, and left over-night. It was then boiled 45 minutes, under a reflux condenser, cooled to 18°C. and filtered off." Innes (1931) points out that this method "would appear to have its limitations, since the boiling certainly alters the chrome complex and, furthermore, would not differentiate, in the freshly tanned leather, between the  $\text{SO}_4$  combined with Cr and that combined with collagen."

### *Sulphur.*

The dried fatty residue from the grease determination is oxidised in the cold with fuming nitric acid (s.g. 1.52) free from sulphuric acid. After standing overnight the solution is evaporated until free from nitric acid and then the sulphur determined as sulphate. The sulphur in the dried fatty residue can be determined very rapidly by the method of Castiglione (1934), which is as follows:—

To the dry residue is added 0.5 g. of solid KCN and 100 c.c. of acetone, and the basin heated on the water-bath until the acetone is completely driven off. The residue is now dissolved

in about 100 c.c. of water, 10 c.c. of 25 per cent. formaldehyde added (Schulek's method of destroying the excess of cyanide) and, after shaking, the solution is acidified with 5 c.c. of conc.  $\text{HNO}_3$ .

The liquid is filtered into a 200 c.c. graduated flask, the fats remaining on the filter being washed with hot water. The solution is made up to the mark, 100 c.c. taken and 5 to 6 drops of 10 per cent. ferric citrate solution and an excess of 0.05N silver nitrate added, the excess of silver nitrate being titrated with 0.05N potassium thiocyanate. From the amount of silver nitrate consumed, the amount of sulphur can be calculated. This, deducted from the weight of original dry residue, gives the amount of fatty matter.

The method is stated to be easy and very rapid, and the results compare very favourably with those obtained by the longer and more difficult methods. No difficulty is found in applying the method to coloured leathers.

For the qualitative detection of free sulphur, a small amount of finely divided leather is heated with acetone and solid KCN. After cooling, the clear liquid is decanted, acidified with a drop of conc.  $\text{HNO}_3$ , and a drop of 10 per cent. ferric nitrate solution added. The characteristic red colour of ferric thiocyanate shows the presence of sulphur.

The following modification of this method has been found satisfactory in the laboratories of the British Leather Manufacturers' Research Association. 10 g. of the finely cut up leather is extracted with acetone in a Soxhlet extractor. The acetone extract is treated with 0.5 g. KCN and refluxed for 1 hour. The acetone is distilled off and the residue dissolved in 100 c.c. distilled water + 10 c.c. 25 per cent. formaldehyde, shaken, and 5 c.c. concentrated  $\text{HNO}_3$  added. The solution is then made up to 200 c.c. and filtered.

To 50 c.c. filtrate excess 0.05N silver nitrate is added + 5 drops 10 per cent. ferric nitrate. The excess silver nitrate solution is titrated against 0.05N potassium thiocyanate solution.

The following method, described by Minatoya, Aoe and Nagai (1935), for the determination of free sulphur in vulcanised rubber, has also been found satisfactory for leather. 10 g. of the leather is extracted with acetone in a Soxhlet extractor, the receiver of which contains about 1—2 g. of KCN. The acetone is distilled off and the mixture of grease, KCN and KCNS is taken up with alcohol (95 per cent.), filtered and washed, whereby the KCNS is separated from the insoluble KCN and grease. The alcohol is boiled off from the filtrate, the residue dissolved in water and titrated as described above.

### *Chromium.*

The chrome leather ash obtained in the ash determination described above is well mixed and then fused with about 3—4 times its weight of a suitable fusion mixture. The heating is conducted over a Teclu burner and should be complete in 20 minutes. The mass should be pure yellow in colour. The crucible is transferred to a beaker containing water and its contents brought into solution by heating. Undissolved matter should be

removed by filtration, re-heated with fusion mixture and then added to the first filtrate. The chromium is now in the form of chromate and can be determined iodometrically as described earlier. If iron is present in the leather then the residue which is insoluble in water after the fusion treatments will be brown. It can be dissolved in HCl and determined.

Aluminium can be determined in the chromate solution by precipitation with ammonia after removal of the iron, as described above by filtration.

To avoid interference by iron with the iodometric titration (if it is not filtered off) the chromate solution can be acidified with phosphoric acid as in the method of Barnebey described under the analysis of chrome liquors.

Suitable fusion mixtures for use in the above fusion are 1 part MgO to 1 part  $\text{Na}_2\text{CO}_3$ , or 1 part  $\text{Na}_2\text{CO}_3$  and 1 part  $\text{K}_2\text{CO}_3$  to 1 part of powdered fused borax.

The Official Methods of the I.S.L.T.C. (*J.S.L.T.C.*, 1924, 62) are as follows:—

Method 1.—The leather ash is transferred to a nickel crucible, 4 cm. diameter, and well mixed with not less than 3 nor more than 10 times its weight of sodium peroxide. The mixture is fused gradually and heated to moderate red heat only, for not less than 1 and not more than 5 minutes. After cooling, the crucible and melt are placed in a large covered beaker, and hot water is poured on which energetically dissolves out the melt. The solution is transferred to a 500 c.c. boiling-flask and, after removing and washing the crucible, a piece of freshly cleaned iron (about 3 cm.  $\times$  1 cm.) is added and the solution boiled 10 minutes. It is cooled, diluted to 500 c.c., filtered through a dry paper and 100 c.c. of the filtrate neutralised with hydrochloric acid, treated with 5 c.c. concentrated HCl in excess and 5 c.c. *N* potassium iodide solution and then titrated with 0.1*N* thiosulphate as usual.

Method 2.—The ash from 5 g. leather is mixed with 3–4 times its weight of a mixture of equal weights of anhydrous sodium carbonate and magnesia in a platinum crucible and then heated to a bright red for 1 minute. The crucible is then cooled, the contents carefully transferred to an agate mortar, ground very intimately indeed until the whole is perfectly homogeneous in colour, and green, yellow and white particles are no longer distinguishable. This mixture is then completely transferred to the platinum crucible and roasted for 10 minutes at a bright red heat, stirring occasionally with a platinum wire. When cool, the pure yellow mixture is dissolved in sufficient dilute hydrochloric acid and then diluted with water to 250 c.c. 50 c.c. are taken, treated with 5 c.c. concentrated hydrochloric and 5 c.c. *N* potassium iodide solution and then titrated with 0.1*N* thiosulphate solution as usual. This method of ignition completely oxidises all  $\text{Cr}_2\text{O}_3$  into chromate and a second roasting should never be necessary.

The International Commission on the Analysis of Chrome Liquors and Leathers proposed to modify the Official Methods (Barcelona, 1923) (*J.I.S.L.T.C.*, 1925, 508) so as to avoid the prolonged boiling to destroy excess of peroxide as follows:—“The

nickel crucible containing the fused peroxide-leather-ash mixture is treated with cold water containing 5 c.c. saturated potassium permanganate solution, shaken and filtered" (Wagner, 1924).

#### *Alkali Metals.*

Woodroffe and Green (1922). Official Method of the I.S.L.T.C. (*J.I.S.L.T.C.*, 1926, 691). The leather is ashed to render chromium compounds insoluble in water, the residue treated with a few drops of sulphuric acid and the excess of acid evaporated off. The ignited residue is extracted with hot water, filtered, and sulphates precipitated in the filtrate in the usual way.

#### *Acid Groups.*

The following types of acid groups are to be found in chrome leathers:—complex combined with the chromium, ionogenically combined with chromium, so called free acid (combined with hydrogen or protein) and alkali salts.

#### *Total SO<sub>4</sub>.*

In the provisional official method of the A.L.C.A., the total SO<sub>4</sub> is determined as follows:—1 g. leather is treated in a flask (250 c.c.) with 200 c.c. 0.1N primary phosphate solution (KH<sub>2</sub>PO<sub>4</sub> or NaH<sub>2</sub>PO<sub>4</sub>.H<sub>2</sub>O), heated for 2 hours in boiling water, cooled, made up to the mark and filtered through a folded filter (rejecting the first 20—25 c.c.). 200 c.c. of the filtrate are placed in a 600 c.c. beaker, 5 c.c. HCl (1 : 1) added, heated to boiling to precipitate the SO<sub>4</sub> with 20 c.c. 1 per cent. BaCl<sub>2</sub>, etc.

#### *Alkali Sulphates.*

A.L.C.A. (Provisional Official). 1 g. leather is treated as above with distilled water instead of primary phosphate solution. 150 c.c. are precipitated with BaCl<sub>2</sub>. 50 c.c. are titrated with 0.01N NaOH against methyl orange, the titration being expressed as SO<sub>4</sub>. If the titration SO<sub>4</sub> be subtracted from the aqueous extract SO<sub>4</sub> then the difference represents the content of alkali sulphate in the leather (as SO<sub>4</sub>).

#### *Free Acid and Combined Acid.*

This can be obtained by subtracting the alkali sulphate from the total sulphate (both determinations are described above). It can also be determined by Meunier and Chambards' Method (1923). 5 g. of finely divided degreased leather is placed in a stoppered vessel together with 50 c.c. 0.2N NaHCO<sub>3</sub> solution and 50 c.c. distilled water. The leather is shaken for 3 hours and the liquor decanted into a 250 c.c. flask. The leather is then shaken for 1 hour with 75 c.c. distilled water, and the extract is added to the 250 c.c. flask. The shaking treatment is again repeated with 50 c.c. distilled water, also adding this extract to the 250 c.c. flask. The contents of the 250 c.c. flask are made up to 250 c.c. and the excess NaHCO<sub>3</sub> titrated using methyl orange or bromphenol blue as indicator. The NaHCO<sub>3</sub> is equivalent to the free and combined acid in the leather. Later work (*J.I.S.L.T.C.*, 1928, 139; 1931, 6) showed that this method was only applicable to leather which had not been dried out.

Merrill, Niedercorn and Quark (1928) use the following titration method in determining the acid groups in chrome leather. 2 g. well divided leather is shaken for 1 hour with 100 c.c. water, allowed to stand overnight, titrated with 0.02N NaOH and methyl orange to pH 5.3, shaken two days more and repeatedly titrated to pH 5.3. The total titration gives the free acid in the leather. The combined acid can be determined on the residual leather by the phosphate displacement method. The basicity of the chrome salt on the fibre can be calculated from the chromium content and the amount of free and combined acid (combined with Cr).

The acid combined with chromium can also be determined by the pyridine extraction method of Gustavson (1927). The well divided leather is shaken with a 4 per cent. pyridine solution (pH = 8) and then washed. Free acid and acid combined with alkali go into solution. The leather retains the  $\text{SO}_4$  combined with the chromium. This can be determined by the phosphate method outlined above. According to Merrill, Niedercorn and Quark (1928) this method of extraction also removes chromium bound acid from the leather. There is no end point to the extraction and there is also the possibility that the pyridine molecules may displace sulphato groups from the chromium complex. Furthermore, the difference in hydrolysability between protein bound and chromium bound  $\text{SO}_4$  is so small that if all the former is removed by neutralisation more will be formed at once by hydrolysis of the sulphato chrome complex. From this it follows that the percentage of protein bound  $\text{SO}_4$  in any leather is a function of the chromium bound  $\text{SO}_4$  content. The method suggested by Merrill and co-workers and described above, is thus empirical and the nature of a compromise, always giving low values for the chromium bound sulphate.

The method described earlier for the determination of the total acid groups in a chrome liquor associated with chromium has been used by Riess and Papayannis (1934) for the determination of the acid groups in chrome leather. An amount of chrome leather (chromed hide powder which had been air dried) corresponding to 2.5 g. of dried substance is heated at 60°C. for 1 hour with occasional shaking with 50 c.c. of approximately 0.1N ammonia in a flask fitted with a reflux condenser and closed with a soda lime tube. The contents of the flask are then filtered rapidly into a measured amount of 0.1N HCl, the leather being washed four times with a little water, first at 60°C. and finally with boiling water, the process taking less than 30 minutes. A control is run alongside, omitting the leather, and this is brought to the same volume as the extract from the leather plus the wash water. Formaldehyde is added next (5 c.c. 40 per cent.), and the solutions titrated with 0.1N or 0.2N alkali as described earlier. The difference in the titration between the control and the leather extract gives a measure of the acid groups in the leather. Where the filtrate is deeply coloured with dyestuffs extracted from the leather, the final titration can be carried out using phenol phthalein as external indicator. It should be again pointed out that ammonium salts in the leather are determined by this method as acid, and that  $\text{SO}_2$  groups are only determined to 50 per cent. due to combination of the  $\text{SO}_2$  with formaldehyde (see below).

If the chrome leather contains mixed acid groups then the  $\text{SO}_4$  groups or Cl groups can be determined separately in the ammoniacal extract plus wash waters.

#### *Oxalates.*

In the case where oxalate groups are present in the chrome leather, the formol-ammonia method cannot be used, due to the dechroming action of ammonium oxalate. In this case, part of the ammoniacal leather extract plus wash waters is determined for  $\text{SO}_4$  or Cl groups and another part is oxidised with  $\text{Na}_2\text{O}_2$  in alkaline solution, acidified with acetic acid and then treated with hot  $\text{CaCl}_2$  solution at the boiling point. The precipitate of calcium oxalate is filtered off after standing 24 hours, dissolved in sulphuric acid and titrated with permanganate. If large amounts of chromium oxalate are present in the leather then it is not completely decomposed by ammonia.

#### *Sulphites.*

After the usual ammonia treatment, the extract is filtered into acidified decinormal iodine solution and this is back titrated with 0.1N thiosulphate. A further preparation of extract is oxidised with  $\text{H}_2\text{O}_2$  acidified and precipitated with barium chloride. This gives  $\text{SO}_4$  groups plus  $\text{SO}_3$  groups and enables the  $\text{SO}_4$  groups to be calculated.

#### *Acid Groups in Glucose Reduced Liquors.*

$\text{SO}_4$  groups are determined gravimetrically as above on part of the ammoniacal leather extract and the ammonia formaldehyde method gives the total amount of acid groups ( $\text{SO}_4$  plus organic acid groups).

#### *Carbonato derivatives.*

The method used by Riess and Papayannis to determine the total acid groups is a modification of that described above by Stiasny and co-workers (*Coll.*, 1929, 567). 10 g. of the wet chromed hide powder (or 2 g. dried material) is heated at  $60^\circ\text{C}$ . as described above with 12 c.c. 0.2N  $\text{NH}_4\text{Cl}$ , 1 g.  $\text{BaCl}_2$  and 50 c.c. approximately 0.1N ammonia (free from  $\text{CO}_2$ ). The extract is filtered rapidly (using a hardened paper) into 25 c.c. 0.1N  $\text{HCl}$ , and the leather residue washed as usual (four washes at  $60^\circ\text{C}$ . to  $100^\circ\text{C}$ .). Filtrate and washes are formol titrated as usual, using a blank as control, with 0.2N  $\text{NaOH}$  ( $\text{CO}_2$  free). The  $\text{SO}_4$  or Cl groups are determined in the extract from another portion of the leather using the formaldehyde ammonia method and filtering into a standard sulphuric acid solution instead of  $\text{HCl}$ , and driving off the  $\text{CO}_2$  before titration. The  $\text{CO}_2$  can be calculated by difference.  $\text{CO}_2$  groups can also be determined direct by decomposing the chrome leather with dilute sulphuric acid (boil) and collecting the  $\text{CO}_2$  in soda lime tubes, passing  $\text{CO}_2$  free air through the apparatus.

#### *Cl Groups.*

The Cl groups can be determined gravimetrically in the filtrate plus washings by making the ammoniacal liquor alkaline. Evaporation, followed by gentle heating to drive off the ammonia and

formaldehyde, gives a residue in which the chlorine can be determined in the usual manner. Titration with 0.1N silver nitrate without ashing gives unsatisfactory results.

*The Composition of the Chromium Salt on the Fibre.*

The methods just described enable the total acid groups in chrome leather to be determined. Recent work by Küntzel and co-workers (1934) gives further information as to the state in which these are present in the leather. It is assumed that well-washed chrome leather contains no free acid and no neutral salts (*i.e.*, acid combined with alkali metals). The acid groups left in the well-washed chrome leather can be regarded as combined as follows:—With the hide substance and with the chromium. The acid groups combined with the chromium can be complex combined and electrovalently combined.

The tests about to be described relate to tannages in which pure chromium chloride or sulphate liquors only were used and attempt to differentiate between the acid groups combined with the hide substance and those combined with the chromium. The determination of the acid combined with the hide substance depends on the principle that hide substance can only take up a definite amount of acid and that this maximum acid combining capacity is easily determined. Hide substance containing acid will take up further acid until this saturation point is reached. The amount of acid at the saturation point, less the amount taken up to reach that point, gives the original amount of acid associated with the hide substance. For this method to be successful in the case of chrome leather it is essential that the capacity of the hide substance to take up acid is not interfered with by the chrome tanning and that the chrome tanning salt in the leather does not take up acid, or that the amount taken up can be controlled. Both of these reservations can be satisfied under certain conditions. For example, the ageing of chrome leather renders the chrome tanning salt less sensitive to the action of acid and lessens the danger of an interaction between it and an acid, particularly in the short time (1 hour's shaking) allowed in the experiments described for the hide substance (hide powder) to take up its maximum amount of acid.

The method used to determine the amount of acid taken up to attain saturation by the dried out chromed hide powder, was as follows:—An amount of chromed hide powder (to correspond to about 2 g. dried weight) which had aged for 8 days was soaked in 25 c.c. distilled water for 30 minutes and then 25 c.c. 0.2N HCl was added. The mixture was shaken for 1 hour and filtered through a dried filter paper and the filtrate determined for acid (titration was to pH = 5.5), using as indicator a mixture of methyl red and methylene blue. The maximum acid uptake of the unchromed hide powder was found to be 0.927M. Equiv./1 g. hide substance. A modified pyridine extraction was used to determine the acid combined with the hide substance together with that associated electrovalently with the chromium. The method was as follows:—The dry chromed hide powder (aged 8 days and approximating to 2 g. hide substance) was shaken for 3 hours with 50 c.c. of 4 per cent. pyridine solution, filtered

and well washed with a little water. The mixed filtrate plus wash water was titrated with 0.1N NaOH (free from  $\text{CO}_2$ ) against phenol phthalein to a deep red. The 4 per cent. solution of pyridine gives a faint pink with phenol phthalein, which one drop of 0.1N HCl will decolorise. The following is an example showing the method of calculation of the analytical results for a chromed hide powder tanned with a 50 per cent. basic chrome alum liquor, and then well washed and air dried:—

Chromium content, 4.91 per cent. on the air dried powder.

Hide substance, 70.2 per cent. on the air dried powder.

Total acid groups (ammonia formaldehyde method), 16.1 c.c. 0.1 N. per 1 g. hide substance.

Acid combined with hide substance and electrovalently to chromium (Pyridine method), 6.45 c.c. 0.1 N. per 1 g. hide substance.

Acid taken up (acid saturation method), 4.43 c.c. 0.1 N. per 1 g. hide substance.

The chromium corresponds to 40.36 c.c. 0.1N thiosulphate per 1 g. hide substance. The total acid (16.1 c.c.) expressed as a percentage on the chromium (40.36 c.c.) is 39.9 per cent., giving a percentage basicity of  $100 - 39.9 = 60.1$  per cent.

The acid combined with the hide substance =  $9.27 - 4.43$  (acid saturation value) = 4.84 c.c. = 12 per cent. of acid expressed on the chromium.

The difference between the pyridine extracted acid (6.45 c.c.) and the acid combined with the hide substance (4.84 c.c.) = 1.61 c.c., gives the acid electrovalently linked with the chromium. This is 4.0 per cent. expressed on the chromium.

The acid which is complex combined with the chromium is the total acid (16.1 c.c.) less the pyridine extractable acid (6.45 c.c.) = 9.65 c.c. or 23.9 per cent. expressed on the amount of chromium.

The following are the results given in the paper for the composition of the chrome salt on the fibre for four experimental chrome tanned hide powders:—

TABLE III.

Composition of the chrome salt on the fibre.	Tannage with chromium chloride liquors.		Tannage with chrome alum liquors.	
	33.3% basic	50% basic	33.3% basic	50% basic
% Basicity	76.9	79.6	63.2	72.1
Complex combined acid	25.6	18.7	37.1	23.9
Electrovalently combined acid	-2.5	1.7	-0.3	4.0

### PRACTICAL CONTROL.

#### General.

Practical control in the tannery, as carried out by a foreman, usually consists in observing the colour changes in the skin during tanning, the rate of penetration of chromium (from a cutting), the flaccidity of the skins (by feel) and the time required to make them stand the boiling test.

If the liquor is too acid, the rate of penetration is rapid, the goods feel plump and are of a very light blue colour, but it takes an unduly long time before they stand the boiling test. If the liquor is insufficiently acid, then it penetrates slowly, the goods, which are deep green in colour, feel flaccid. Sometimes the chrome begins to precipitate and the skins become spotted on the grain with subsequent trouble in dyeing. A difference in shade in a cut section of a chrome leather indicates a difference in basicity, the bluer or darker the cut, the more basic the tannage.

### *Shrinkage Temperature.*

The progress of the chrome tanning process can be followed by observing the shrinkage temperature, that is the temperature at which the chromed material shrinks when heated in water. A strip of the wet leather about 5 cm. long and 3 mm. wide is fastened to a thermometer so that the middle of the strip is situated alongside the mercury bulb of the thermometer. The thermometer with attached leather is placed in a beaker of water and the temperature slowly raised. The temperature at which the leather commences to curl is the shrinkage temperature.

### *Boiling Test.*

The process of chrome tanning is usually considered to be complete when the leather stands the boiling test, that is, when it does not shrink if kept in boiling water for a definite time, which varies between 1 and 10 minutes with different operators. The time specified by the United States Government for finished lace leather is 5 minutes. Five minutes is the time used by the British Leather Manufacturers' Research Association. It is a fact, however (Stiasny, *Gerbereichemie*, pp. 487, 488) that a large number of first class commercial chrome leathers do not stand the test. Stiasny states that commercial two-bath chrome leathers, with very few exceptions, do not stand the boiling test. The shrinkage temperature for quite a number of these leathers is as low as 86°C., and in the majority about 92°C. This statement, it will be noted, applies mostly to two-bath leathers. Furthermore, in some cases the leathers immediately after tanning do not stand the test but after the later processes of horsing, washing, neutralising, etc., the finished leather stands the test, and *vice versa*. Elöd and Cantor (1934) state that it is a well-known fact that most leathers after drying in the finished condition give a poor boiling test result, and that there are many leathers which are otherwise satisfactory which do not give an absolutely satisfactory boiling test before being dried out. There is also the case of leather which before storage stood the test but does not do so after a time. In some tanneries, the working policy is to carry out the tannage so that the leather stands the test after being neutralised rather than run the risk of over-tannage of the grain by driving the tannage too far or running the risk of over-neutralising. The question also arises as to whether the leather which stands the boiling test is better and wears better than the leather which does not stand the test.

According to Burton (1920) the leather should be neutralised before being subjected to the boiling test, the completion of tannage being best judged from the feel of the sample (absence of horniness and curling at the edges). The boiling should be for 5 minutes.

Lamb (*The Manufacture of Chrome Leather*, p. 171) expresses the opinion that it is extremely important that the leather should stand the boiling test before the goods are finally removed from the drum.

The details of the method of carrying out the boiling test are also of importance. For example, according to Stather (1934), chrome leather which when brought into water at 100°C. does not stand the boiling test, has been found to do so if placed in water at 50°C. and the temperature slowly raised to 100°C. Elöd and Cantor (1934) describe some experiments in which gelatin discs were treated with various chromium compounds. The resulting products stood the boiling test provided the chromed material was placed in water at 100°C., the period of the test being 5 minutes, whereas the same chrome tanned gelatin discs were completely dissolved in 1 minute in water at 42°C. The chromed gelatin discs, before the boiling test at 100°C., were of various colours, red, yellow, violet, etc., but after the treatment at 100°C. all the samples had become green.

According to Hudson (1927), the boiling test is not always a satisfactory measure of the completeness of tanning. The results of the test depend not only on the chromium content of the leather but also on the acid groups present. Leather tanned with a basic chromium chloride liquor will fail to stand the test, irrespective of the chromium content of the leather. Leather tanned with a basic sulphate liquor, to which neutral chlorides have been added, will show a lessened stability to the test, the extent of which will depend on the concentration of neutral chlorides. In the case of leather which stands the boiling test at the end of tanning and fails when finished, this may be due, according to Hudson, to the replacement by monovalent groups of the divalent groups originally present, *e.g.*, the replacement of  $\text{SO}_4$  by fatty acids during the fat-liquoring process. This applies to both one- and two-bath leathers. Monovalent groups, inorganic or organic, reduce the stability of chrome leather to the boiling test. Hudson advanced the following hypothesis regarding the state of combination between the chromium compound and collagen to explain this effect. In chrome leather containing divalent groups there are two types of combination between the chromium salts and the collagen: (1) a compound in which the chromium atom is attached by primary valency to the carboxyl groups of the collagen; (2) a compound in which the chromium atom is indirectly attached to the amino groups by means of the divalent group. Replacement by chlorides of part of the divalent groups combined with chromium results in a lessened stability to the boiling test. In fat-liquoring, fatty acids replace the divalent groups to some extent with the same effect on the boiling test.

Another striking feature relating to the boiling test has been pointed out by Gustavson (1931), namely, that excessive re-tannage of chrome leather by vegetable tannins has a de-tanning

effect, as judged by the loss of tensile strength, the character of the grain and the boiling test. Gustavson found that re-tannage of a leather tanned by a commercial chrome extract, in solutions of straight wattle bark extract, gave a leather without acid sulphate present in the chrome complex. The acido groups had been displaced by the vegetable tannin with the development of instability to the boiling test and loss in tensile strength. The same re-tanning of a leather of nearly the same chromium content, but previously tanned in a sucrose-reduced chrome liquor, caused no alteration to the chrome tannage (the acidity of the chrome complex was not altered, the tensile strength and the boiling test remained satisfactory). By the re-tanning of this chrome leather from the sucrose-reduced chrome leather tannage with sulphited quebracho extract, the sulphato groups in the chromium complex could eventually be removed, but even in this case the leather was not detrimentally affected. This is probably because of the penetration of the sulphited groups of the quebracho into the complex.

Over-neutralising can render a satisfactory chrome leather unsatisfactory according to the boiling test. Dyeing and fat-liquoring do not usually alter the boiling test resistance, although the use of certain fat-liquors and certain dyestuffs in excess can. The method of drying the leather can also be detrimental; a sharp drying reducing its resistance to the boiling test, whilst drying at a moderate rate has no such effect. This is particularly shown up if the boiling test be applied directly to the dried leathers without previously soaking them back in cold water. Glazing can also affect chrome leather, as shown by the boiling test, but it is uncertain as to whether this is due to the glaze or the heat of the glazing operation.

After tanning it is usual and beneficial to horse or pile the goods for a few days. The tannage proceeds further, the leather resists the boiling test better, the amount of chromium salts removed by subsequent washing lessens, and the leather becomes more resistant to the action of acids. Apparently the changes which occur are similar to those which occur to precipitated chromium hydroxide or highly basic chromium salts, namely, olation. This explains why chrome leather immediately after tanning is more sensitive to alkalies and acids than after storage for a time. Furthermore, the free acid content of a chrome leather increases on ageing and the basicity of the chrome salt increases. Thus olation processes are proceeding in chrome leather whereby the highly basic salt olates further, disturbs the hydrolysis equilibrium to give more basic chrome salt and free acid. This setting free of acid, as in horsing up, should take place before neutralising and not after.

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## PART II.

# Chromium Salts and Chrome Tanning from a Theoretical Aspect.

### CHAPTER VI.

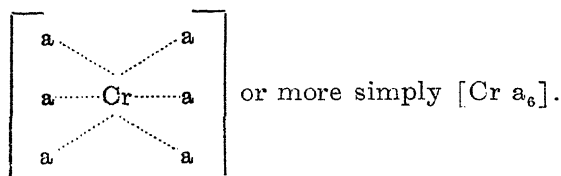
#### THE CHEMISTRY OF CHROMIUM SALTS.

##### (i) AN OUTLINE OF THE WERNER CO-ORDINATION THEORY OF VALENCY.

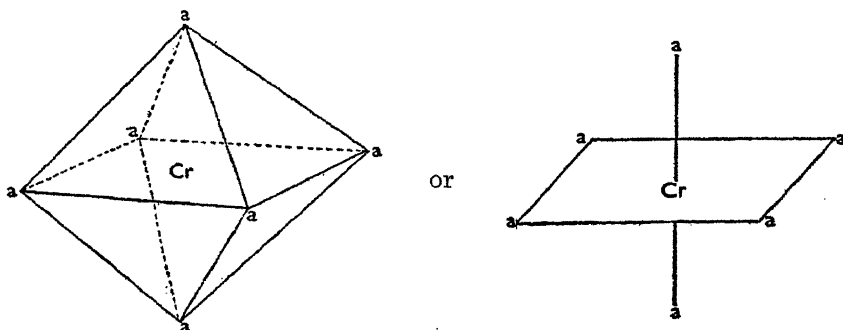
ONE of the most important factors in the recent development of the chemistry of chromium compounds has been the Werner co-ordination theory, which was first suggested in 1891 and developed more fully in 1893. It is proposed to give but a brief outline of this theory, which will, however, be sufficient for this report, and the reader desiring a fuller account is referred to the *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, 5th Edn., by A. Werner, revised by P. Pfeiffer, 1923. An English translation of an earlier edition of this book can also be obtained.

The term "valency" in the early days of its use was defined as the combining power of an element in terms of monovalent atoms (hydrogen being taken as a monovalent standard or oxygen as a divalent). The chromium atom, for example, was stated to be trivalent in that it combined with three monovalent chlorine atoms in the compound  $\text{CrCl}_3$  (chromium trichloride). Considerable difficulty arose, however, in formulating the constitutional formula of so-called "molecular" or complex compounds formed by the combination of apparently saturated molecules, such as, for example,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  or hydrated chromium trichloride, which does not give up its water when kept in a desiccator over sulphuric acid. Further difficulties arose in explaining the existence of more than one chromium trichloride, the different trichlorides ionising differently when dissolved in water, one trichloride giving three chlorine ions, another giving two chlorine ions and a third one chlorine ion per single chromium atom. It appeared to Werner that some atoms (in the examples just described, chromium) are capable of exerting two different types of valency, (1) the ordinary primary or principal valency, which for chromium is three, and (2) a new type of auxiliary or co-ordinative valency by which the central atom surrounds itself by a number of atoms, radicles or co-ordinated groups, as they are called, forming a complex ion, the atoms held by the principal valencies being situated without the complex. For example, in the case of hydrated chromium trichloride, there are three principal valencies for chromium, and these are occupied by the three chlorine atoms, whereas the water molecules are linked by auxiliary valencies. Werner further introduced a simple graphic method of representing the formulæ of substances containing both auxiliary and principal valency

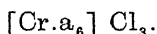
linkages. In this method, the auxiliary valency groupings (six in number for chromium) are shown associated with the chromium atom, and form with it a complex ion, the whole being bracketed as shown, the auxiliary linkages being denoted by dotted lines.



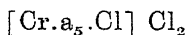
The corresponding space formation for the complex chromium ion is as follows:—



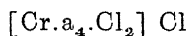
The square brackets in the first illustration are a conventional method used to denote the various chemical groups which are linked co-ordinatively with the chromium atom. In the case of hydrated chromium trichloride the six "a" groups in the complex are all water molecules and the complex ion is capable of principal valency linkage with the three Cl atoms. These principal valencies, it should be noted, are ionised. In writing a chemical formula for chromium compounds the atoms, groups or radicles joined by principal valency linkages, which are ionised in aqueous solution, are shown outside the brackets, as below:—



In water, such a salt would ionise into the complex chromium kation, carrying three positive charges,  $[Cr.a_6]^{+++}$  and three chlorine ions, each negatively charged. The other chromium trichlorides mentioned above are formulated on this scheme as follows:—



which ionises giving two chlorine ions and the complex chromium kation  $[Cr.a_5.Cl]^{++}$ , and



which gives one chlorine ion and the complex chromium kation  $[Cr.a_4.Cl_2]^+$ .

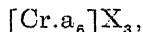
The number of monovalent atoms or radicles or other groups, such as  $\text{H}_2\text{O}$ ,  $\text{Cl}$ ,  $\frac{1}{2}(\text{SO}_4)$ ,  $\text{NH}_3$ , associated with the central atom and contained in the complex gives what is called the co-ordination number of the central atom, which in the case of chromium, as already mentioned, is 6. It should be noted that one divalent group counts as two monovalent groups. These groups co-ordinated or associated with the central atom no longer give their characteristic ionic reactions and are, therefore, described as "masked."

In developing this new conception of valency, Werner found it necessary to introduce a new nomenclature for describing the different chromium salts. The following are the general principles underlying this system:—

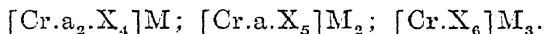
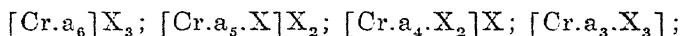
- (1) When the complex is kationic, that is positively charged, the naming of the compound starts with the acid groups within the complex,  $\text{Cl}$  being referred to as "chloro,"  $\text{SO}_4$  as "sulphato,"  $\text{SO}_3$  as "sulphito,"  $\text{CO}_3$  as "carbonato,"  $\text{C}_2\text{O}_4$  as "oxalato," and so on. Then follow such co-ordinated groups as  $\text{H}_2\text{O}$  ("aquo"), oxygen ("oxo"),  $\text{OH}$  ("hydroxo"). The metallic element (chromium) comes next and is referred to as "chromi" (for trivalent chromium). Following the full description of the complex kation come the customary names of the acid radicles not present in the complex, *e.g.*, pentaquo-hydroxo-chromi-sulphate  $[(\text{H}_2\text{O})_5.\text{Cr}.\text{OH}]\text{SO}_4$ .
- (2) If the complex is neutral, that is, not charged, the name ends with that of the metallic element, *e.g.*, trichloro-triaquo-chromium  $[(\text{H}_2\text{O})_3.\text{Cr}.\text{Cl}_3]$ .
- (3) When the complex is anionic, that is, negatively charged, the name of the compound commences with that of the kations not present in the complex; then follows the description of the complex, concluding with the termination "ate," *e.g.*, tri-sodium hexachloro-chromiate  $[\text{Cr}.\text{Cl}_6]\text{Na}_3$ .

Other new terms will be illustrated as they are met with.

Under the Werner valency concept, chromium salts can be divided into seven classes or types. These can be illustrated by starting with the first type, the normal chromium compound:—



and developing therefrom the remaining six of the series. These can be represented graphically by the following formulæ where X represents a monovalent group and M a monovalent metal or hydrogen:—



Each of these types will be considered in turn.

It is of interest at this stage to draw attention to the following points relating to the above series. In solution in water a compound of the type  $[\text{Cr}.\text{a}_6]\text{X}_3$  ionises into the ions  $[\text{Cr}.\text{a}_6]^{+++}$  and  $3\text{X}^-$ , that is, the complex chromium ion and three non-metallic ions,  $\text{X}^-$ . If the chromium complex should contain an acid group, such as  $\text{SO}_4$  or  $\text{Cl}$ , then this acid group or groups is not ionised

as such and if (in acid solution)  $\text{BaCl}_2$  or  $\text{AgNO}_3$  be added, is not precipitated as  $\text{BaSO}_4$  or  $\text{AgCl}$  respectively. That is, the  $\text{SO}_4$  or  $\text{Cl}$  within the complex does not behave as a simple ion but is linked up to the chromium atom, *i.e.*, masked, forming part of a complex ion. If now the series be followed, the nature of the ionisation changes stage by stage. The number of monovalent non-metallic ions outside the complex lessens and at the same time the nett electric charge on the complex chromium ion also lessens, until a stage is reached where no ionisation occurs, namely, at the neutral compound  $[\text{Cr}.\text{a}_3.\text{X}_3]$ . Beyond this stage, the compounds in the series again ionise but it is now found that the ion outside the complex is metallic and kationic and that the electric charge of the complex chromium ion has changed to anionic. This point must be borne in mind when the behaviour of chromium salt solutions in electrophoresis experiments is studied, for in the cases where the chromium complex is kationic it will proceed under the influence of the electrical current in the opposite direction to that where it is anionic. In many solutions of chromium salts both classes of chromium ions are present.

Each of the above types will now be considered in turn, but only in so far as examples are available which are of particular interest.

*1st Type.*— $[\text{Cr}.\text{a}_6]\text{X}_3$ . “a” can be one of many neutral groups, such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , etc., and “X” is an acidic group such as  $\text{Cl}$ ,  $(\text{SO}_4)_\frac{1}{2}$ . All the substances in this class ionise into a trivalent complex chromium kation and three monovalent anions or their equivalent. Of particular interest from a tanning standpoint are the compounds in which “a” is  $\text{H}_2\text{O}$ , *i.e.*, aquo, or more precisely, hexaquo compounds, and “X” represents any acid group, for example,

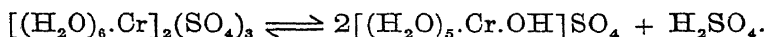
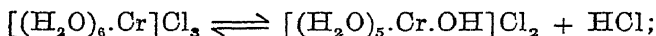
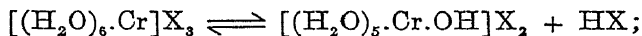
chromium trichloride  $[(\text{H}_2\text{O})_6.\text{Cr}]\text{Cl}_3$ ;

chromium sulphate  $[(\text{H}_2\text{O})_6.\text{Cr}]_2(\text{SO}_4)_3$ ;

chrome alum  $[(\text{H}_2\text{O})_6.\text{Cr}]_2(\text{SO}_4)_3.\text{SO}_4.\text{K}_2.12\text{H}_2\text{O}$ .

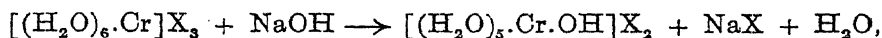
Aqueous solutions of hexaquo salts with colourless anions are generally violet because of the kation  $[(\text{H}_2\text{O})_6.\text{Cr}]^{+++}$ .

Hexaquo salts hydrolyse in aqueous solution as follows:—

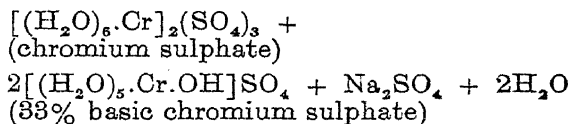


The compound formed containing OH in the chromium complex is a hydroxo chromium compound. In addition, free acid (HX) is a product of the hydrolysis of chromium salts. The hexaquo chromium ion,  $[(\text{H}_2\text{O})_6.\text{Cr}]^{+++}$ , has no tanning action and any tanning action exerted by salts in this class is to be attributed to the products of their hydrolysis, namely, ions in which the hydroxyl group has replaced  $\text{H}_2\text{O}$  in the complex, reducing the positive charge by one unit. It will be shown later that the hydroxo salts so formed and, in particular, substances produced from them by a process known as olation, are probably the materials which are active in bringing about chrome tanning.

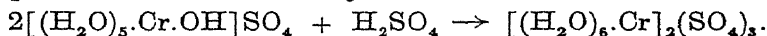
*2nd Type.*  $[\text{Cr.a}_5.\text{X}]\text{X}_2$ . Salts of this type are usually, though not always, green. They ionise into the divalent complex chromium kation  $[\text{Cr.a}_5.\text{X}]^{++}$  and the two monovalent anions. The most important sub-group in this type covers the hydroxo-pentaquo salts, *i.e.*,  $[(\text{H}_2\text{O})_5.\text{Cr.OH}]\text{X}_2$ , of which the sulphate,  $[(\text{H}_2\text{O})_5.\text{Cr.OH}]\text{SO}_4$ , is a good example, this being the 33 per cent. basic salt so largely used in chrome tanning. The preparation of the hydroxo-pentaquo salts, *i.e.*, type 2, from the hexaquo chromium salts (type 1) can be brought about as follows by the addition of alkali:—



a process so well known in the tannery as “making a liquor basic,” a typical example of which is the making of a 33 per cent. basic chrome liquor from chromium sulphate or chrome alum with caustic soda as follows:—



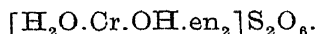
The process can be reversed by the addition of acid, as follows:—



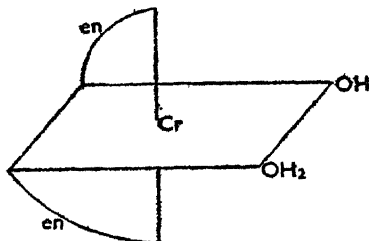
Thus the basicity of a chrome liquor would appear to be under complete control and to be capable of being regulated as desired by the addition of acid or alkali as found necessary. This rapidity of interaction between the hydroxo groups and acid is made use of by the chemist in determining the amount of such groups in a chrome tanning liquor and thereby obtaining some information relating to its tanning properties. This will be referred to later. If, however, sodium hydroxide be added to a solution of chromium trichloride until precipitation is just about to commence and the mixture allowed to stand, the pH value falls and more alkali can be added without causing precipitation. This intermittent addition can be repeated until about 2.5 molecules of alkali have been added per atom of chromium. Bjerrum found that basic chromium chlorides on standing or by heating undergo a change leading to the formation of bigger molecules. He assumed that the hydroxo compounds first formed are gradually converted into compounds in which the OH groups can no longer be easily attacked by acids.\* Such compounds are called “Ol” compounds and the process “olation.” This process is, according to Stiasny, of great importance in the chemistry of chrome tanning. Stiasny considered the changes which basic chromium salts undergo on standing or by heating, etc., in the light of the former investigations of Werner and Pfeiffer, and found that, by so doing, many observations in the laboratory could be explained and new light thrown on the mechanism of chrome tanning. The olation process will receive further consideration later under the section dealing with basic chromium compounds but it does not seem out of

\* Bjerrum did not give any structural explanation to this change neither did he use the words ol-compound or olation nor attribute the formula of ol-compounds or the process of olation to these changes.

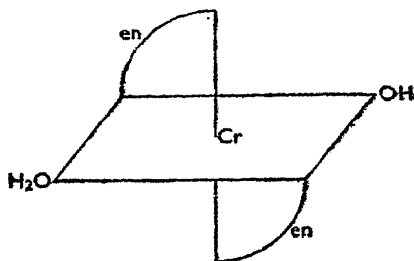
place to illustrate what it is at this stage. An admirable material for the purpose is hydroxo-aquo-dien-chromi-dithionate, which can be formulated:—



“ en ” in these formulæ is a conventional contraction for ethylene diamine. Two isomeric forms of this substance are known and their structures within the chromium complex can be represented by the following space formulæ:—

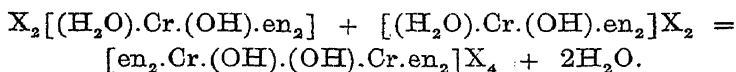


known as the “ cis ” form and in which it is to be noted that the OH and OH<sub>2</sub>, i.e., H<sub>2</sub>O, groups are *adjacent*, and



known as the “ trans ” form. It is here emphasised that the OH and H<sub>2</sub>O groups are *not adjacent*.

The properties of these two isomers are entirely different. The “ cis ” form, in which the OH and H<sub>2</sub>O groups are adjacent, on heating or allowing to stand gives up water (H<sub>2</sub>O groups) and forms a substance containing two chromium atoms within the complex:—



The water molecule which was linked to the chromium atom by an auxiliary valency has been substituted by the hydroxo group of another molecule. Such poly-chromium complex compounds are extremely important from a tanning standpoint.

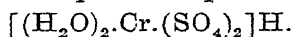
According to Stiasny (1931), they contain hydroxo groups which are linked up on the one hand to a chromium atom by a principal valency and on the other hand to a second chromium atom by means of an auxiliary valency.

*3rd Type.*— $[\text{Cr}.\text{a}_4.\text{X}_2]\text{X}$ . These salts ionise into two ions only, a complex monovalent chromium kation and a single monovalent anion. Of particular interest from a tanning standpoint are dihydroxo-tetraquo-chromi-chloride  $[(\text{H}_2\text{O})_4.\text{Cr}.\text{OH})_2]\text{Cl}$  and dihydroxo-tetraquo-chromi-sulphate  $[(\text{H}_2\text{O})_4.\text{Cr}.\text{OH})_2]\text{SO}_4$ . The former is the 66.7 per cent. basic chromium chloride and the

latter the 66.7 per cent. basic chromium sulphate. Reference is also made to the latter substance in Chapter VII, where it forms the basis of a suggested theory of chrome tanning.

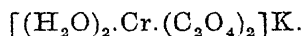
*4th Type.*— $[\text{Cr.a}_3.\text{X}_3]$ . Substances of this type are not ionised and many of them are insoluble in water. Of importance from a tanning aspect may be mentioned the substance of the formula  $[(\text{H}_2\text{O})_3.\text{Cr.}(\text{SO}_4)_{3/2}]$ , which is present, at any rate temporarily, in many heated chromium sulphate liquors, and the substance hydroxo-oxalato-triaquo-chromium,  $[(\text{H}_2\text{O})_3.\text{Cr.}(\text{OH}).(\text{C}_2\text{O}_4)]$ , which forms the chief constituent of a tanning liquor prepared from an equimolecular mixture of chromium trichloride, sodium oxalate and sodium hydroxide. Freshly prepared chromium hydroxide  $[(\text{H}_2\text{O})_3.\text{Cr.}(\text{OH})_3]$  can also be considered as belonging to this type. Küntzel, Riess and co-workers (1934) suggest that chrome leather contains chromium complexes of the general formula  $[\text{Cr.a}_3.\text{X}_3]$ .

*5th Type.*  $[\text{Cr.a}_2.\text{X}_4]\text{M}$  (where M is an alkali metal). In this type and the types which follow, the electric character of the ions has become such that the chromium complex is now the anion and the ion outside the complex is kationic and, in general, metallic. The chromium and any acid groups within the complex are masked, and the addition of ammonia or other alkalis in small amounts brings about no precipitation of chromium until the complex is broken up. A good example of the above type is the following acid, disulphato-diaquo-chromi acid,



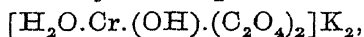
This is one member in a series of similar substances which are produced by heating normal chromium sulphate, especially after adding a little sulphuric acid to retard hydrolysis changes. In fact, the whole transformation from normal or hexaquo-chromi-sulphate to an acid belonging to type No. 7 proceeds, accompanied by hydrolysis changes, when concentrated chromium sulphate solutions are boiled. If the boiled solution is diluted and allowed to stand for a time, the above process reverses and water gradually displaces the  $\text{SO}_4$  from the complex. The two processes, the entrance of  $\text{SO}_4$  groups into the chromium complex in hot concentrated solutions and the displacement in cold diluted solutions are typical for chromium sulphate and substances containing chromium sulphate, such as chrome alum. The evaporation of chromium sulphate with potassium sulphate or the evaporation of a chrome alum solution brings about the formation of chromium complexes similar to those just described in which the  $\text{SO}_4$  is completely masked. Such a solution, on standing, slowly loses the properties brought about by concentration. Stiasny, Gergely and Dembo (1931) were able to show that commercial solid chromium sulphate and chromium sulphate tanning extracts contain anionic chromium complexes with chromium and  $\text{SO}_4$  groups which are masked.

A further substance of this type which is of importance in that it can be used for giving the grain a preliminary treatment protecting it against later liquors but which does not, of itself, give leather which will withstand the boiling test, is given by the following formula:—



This salt is produced by the reducing action of oxalic acid upon potassium dichromate (Croft, 1842).

*6th Type.*  $[\text{Cr.a.X}_5]\text{M}_2$ . An interesting member of this type is dipotassium-dioxalato-hydroxo-aquo chromiate,



which is produced from the mono-potassium salt described under the previous type by the addition of potassium hydroxide. This substance occurs in two isomeric forms and it is of note that the "cis" form, i.e., in which OH and  $\text{H}_2\text{O}$  are adjacent, undergoes olation, the Ol compound produced containing two chromium atoms in the complex.

*7th Type.*  $[\text{Cr.X}_6]\text{M}_3$ . Hexa-acido-chromiates do not tan but may be converted into tanning materials by the addition of alkali, which alters the complex.

## (ii) AN OUTLINE OF THE ELECTRONIC THEORY OF VALENCY.

Having dealt with the principal points in the Werner theory of valency, an outline of the electronic theory of valency will next be presented. The electronic theory, a full account of which is given in *The Electronic Theory of Valency* (1927), by Sidgwick, and in *Recent Advances in Physical Chemistry* (1931), by Glasstone, enables chemical reactions and the structure of molecules to be examined from a new standpoint. It will be shown in this report to provide the interpretation of the Werner valency theory.

The electronic theory of valency is based upon the fundamental idea that all matter is composed of electricity. The electricity is of two kinds, positive and negative. Each kind is made up of tiny particles, the negative ones or electrons are all exactly alike and the positive ones or protons are similarly all alike. An electron at a certain distance repels another electron with a certain force; protons at the same distance apart also repel each other with the same force, while a proton and an electron at the same distance attract one another with exactly that same force. These particles are natural units of electricity of two related and yet opposite qualities. Electrons are very light and very mobile, whereas a proton weighs 1840 times as much as an electron and, hence, is very much harder to set in motion.

Protons and electrons attract one another strongly and in various combinations form the atoms or elements, of which there are nearly a hundred different kinds. According to the electronic theory, an atom is considered to consist of a small positively charged nucleus containing the whole positive electricity of the atom and practically the whole of its mass (since the protons are so much heavier than electrons) and this is surrounded by a number of negatively charged particles (electrons) which form with it a neutral atom, that is, the positive and the negative charges are equal in number. The electrons surround the nucleus in a series of successive orbits, sheaths or layers, the outermost orbits being responsible for practically the entire volume occupied by an atom. For example, the atom of hydrogen, the lightest and simplest of the elements, contains one proton and one electron (and, therefore, only a single sheath). Although they attract strongly, the proton and electron are not drawn into immediate

contact but the electron moves in an orbit round the proton (in a similar manner to the movement of the earth round the sun). Their distance apart is very small, being of the order of one two-hundred millionth part of a centimetre. If the size of an atom of hydrogen is taken to be the diameter of the orbit in which the electron revolves round the proton which forms its nucleus, then the diameter of the electron is only one hundred-thousandth part of this.

The next element to hydrogen in atomic weight is helium (atomic weight 4). The atom of helium has a nucleus containing 4 protons and 2 electrons and has, therefore, a nett positive charge of  $4 - 2 = 2$ . Its atom is completed by two electrons which revolve round the nucleus at a distance (comparatively speaking). These are the orbital electrons of the atom. To give another example, the atom of lithium has a nucleus containing 7 protons and 4 electrons, and 3 orbital electrons.

Every atom has a nucleus which is heavy and relatively motionless round which revolve a number of electrons. The nett positive charge of the nucleus, or nuclear charge, is a whole number, which is equal to the number of its orbital electrons. This is known as the atomic number of the element in question. The atomic number of an element is also the ordinal number of the element in the series of elements arranged according to their atomic weights. It is at once the ordinal number of the element, the positive charge on the nucleus and the number of electrons surrounding the nucleus. The atomic numbers indicate the properties of each element and are more fundamental than the atomic weights (see below). The electrons in the nucleus act as a binding force to hold the protons together and prevent them flying apart. Their number is never less than one-half the number of protons in the nucleus. The following table gives the atomic number and the components of the nucleus for several common elements.

TABLE IV.

THE ATOMIC NUMBER AND COMPONENTS OF THE NUCLEUS FOR VARIOUS ELEMENTS.

Element.	Atomic number.	Components of the nucleus.		Atomic weight or mass number.
		Protons.	Electrons.	
H	1	1	0	1
He	2	4	2	4
C	6	12	6	12
O	8	16	8	16
Na	11	23	12	23
Cl	17	35	18	35
		37	20	37
		39	22	39
Ca	20	40	20	40
Cr	24	52	28	52
Cu	29	63	34	63
		65	36	65
Pb	82	206	124	206
		207	125	207
		208	126	208
		209	127	209

It will be seen from the above table that it is possible for one element to have more than one kind of atom, the nucleus being compounded in various ways. The different kinds of atom for the same element are called "isotopes." They have the same atomic number but different atomic weights. Chlorine, for example, has three isotopes (atomic weights 35, 37 and 39), copper has two and lead has four (atomic weights ranging from 206 to 209), mercury has seven isotopes and tin has eleven. The chemical properties of isotopes are quite indistinguishable. This is explained by the fact that the chemical properties of the different elements are directly determined, not by the nuclei, but by the outmost orbital electrons. Ordinary chemical reactions do not involve the nucleus at all.

Some attempt is made in the diagrams which follow,\* to give a picture of the arrangement of the orbital electrons for a number of elements, firstly arranged in the order of their orbits (Fig. 1) and secondly as models showing roughly certain features in the arrangement of the electrons (Fig. 2).

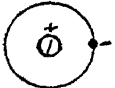

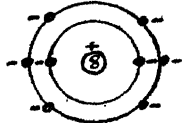
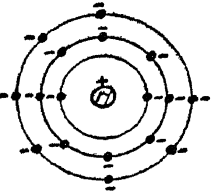
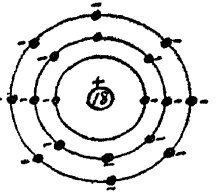
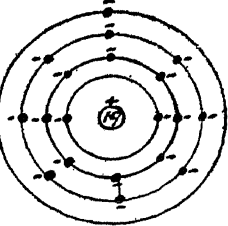
<u>Orbital Electrons</u> <u>arranged in order of their orbits</u>		
 <p>Hydrogen (1) Atomic Number 1</p>	 <p>Helium (2) Atomic Number 2</p>	 <p>Oxygen (2.6) Atomic Number 8</p>
 <p>Chlorine (2.8.7) Atomic Number 17</p>	 <p>Argon (2.8.8) Atomic Number 18</p>	 <p>Potassium (2.8.8.1) Atomic Number 19</p>

FIG. 1.

In an atom magnified so that the electrons appear as big as sixpences (their shape is not known), the protons would be scarcely visible, the nucleus, according to the particular atom, might be anything in size up to a football. Round this the electrons would

\* The author is indebted to Prof. James Kendall's "At Home Among the Atoms," 1932, for these diagrams.

be revolving, the nearest a few feet away and the farthest or outermost (the valency electrons), those which take part in chemical combination, moving in orbits which at their greatest distance would be from half a mile to a mile away. The other electrons would lie between.

For most atoms it is very easy to subtract an electron or add an electron. To do this a second time is not so easy, as the result of the first operation is to leave the atom electrically charged. Interchanges of electrons between different atoms constitute chemical action. It is, however, exceedingly difficult to change the nett positive charge of the nucleus and thereby bring about transmutation of the elements, although this has been done and is occurring naturally with radio active elements such as radium. That is to say, the essence and individuality of an atom resides in the nucleus. When this is altered a new element is formed.

### Spatial Arrangements of the orbital electrons.

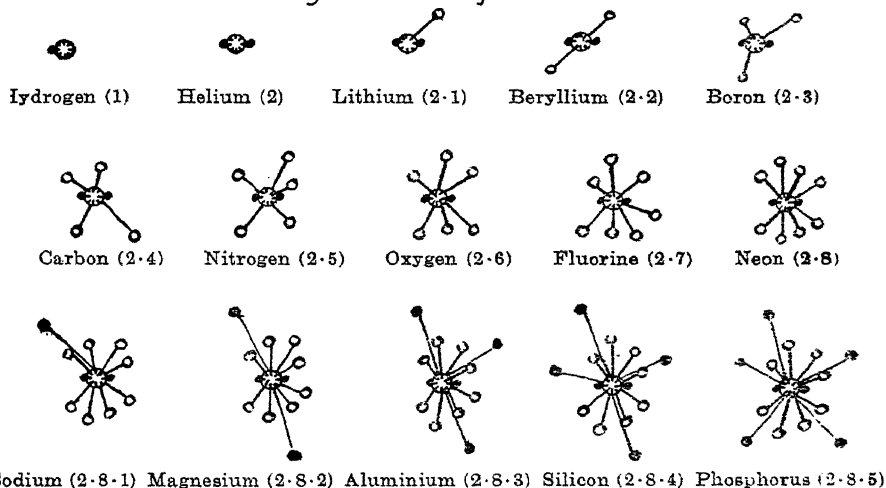


FIG. 2.

Chemical and physical properties (apart from mass effects) are determined by the number and shape of the electronic orbits, especially of those farthest from the nucleus, for when two atoms approach one another these external orbits are first affected. If an equal number of protons and electrons were added to a nucleus, its mass would increase while its nuclear charge would remain unaltered. This would give an isotope (see Table IV). Thus two isotopes have the same number of planetary electrons and the same nuclear charge. The difference in the mass of the nucleus has only a very small effect on the chemical and physical properties and can only be detected with difficulty. Very little is known of the structure of the nucleus. However, this has only an indirect bearing on chemical questions and is not discussed further in this report.

Electrons not contained in the nucleus are assumed to be in rapid motion around the nucleus, each travelling in a regular orbit

(a kind of solar system), the motion of each electron being made up of two superimposed motions, a simple orbital motion and a slower rotation of this orbit round the nucleus. In hydrogen, with only one electron, this occupies what is known as a  $1_1$  orbit or first sheath. In helium, with two electrons, each occupies a  $1_1$  orbit or the first sheath. If a third electron be introduced (as in lithium) then this (due to forces of repulsion) takes up an elliptical orbit designated  $2_1$ , which for one part of its path is inside the orbits  $1_1$ , while the rest is outside. A  $2_1$  orbit or sheath is much larger than a  $1_1$  orbit and the work required for the removal of the electron in this orbit is less. Proceeding from helium to neon involves the building up of a group of eight such electronic orbits. Some of these are ellipses and are designated  $2_1$  and some are circles designated  $2_2$ . These orbits comprise what might be generally termed a second sheath. Other similar sheaths follow naturally as the atomic numbers increase. These are illustrated diagrammatically in Figs. 3 and 4. Fig. 3 shows the development of the various circular and elliptical orbits from the atom of hydrogen to the atom of sodium, and Fig. 4 takes the formation of the various orbits still further, i.e., to orbit  $4_4$ .

THE DEVELOPMENT OF THE VARIOUS ORBITS FROM HYDROGEN TO SODIUM.

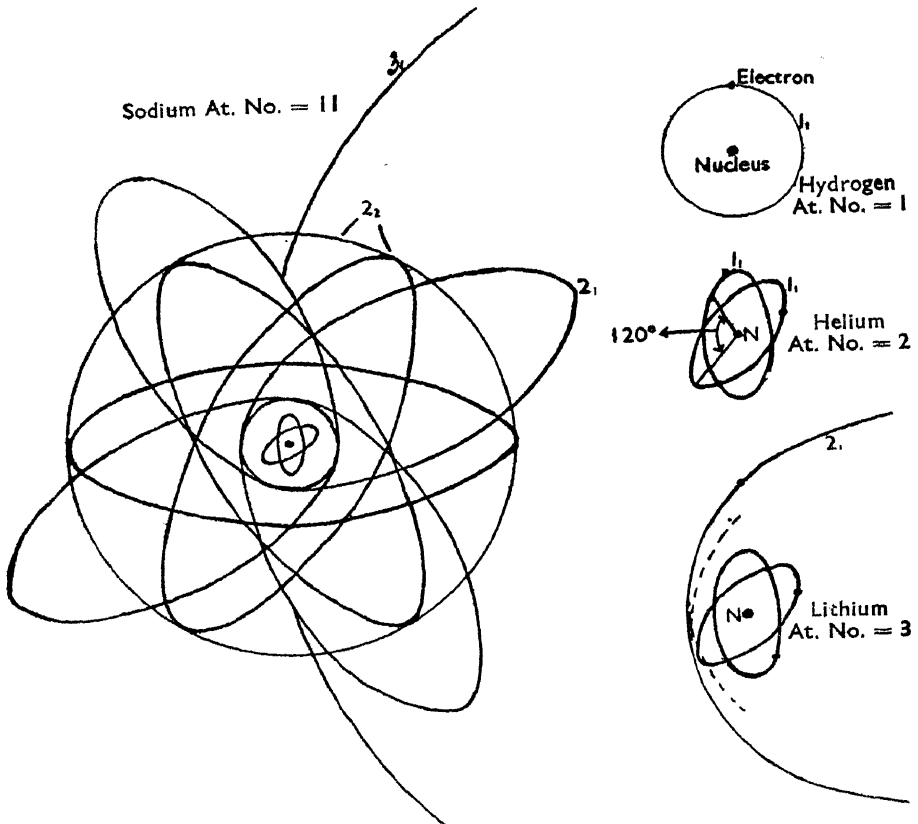
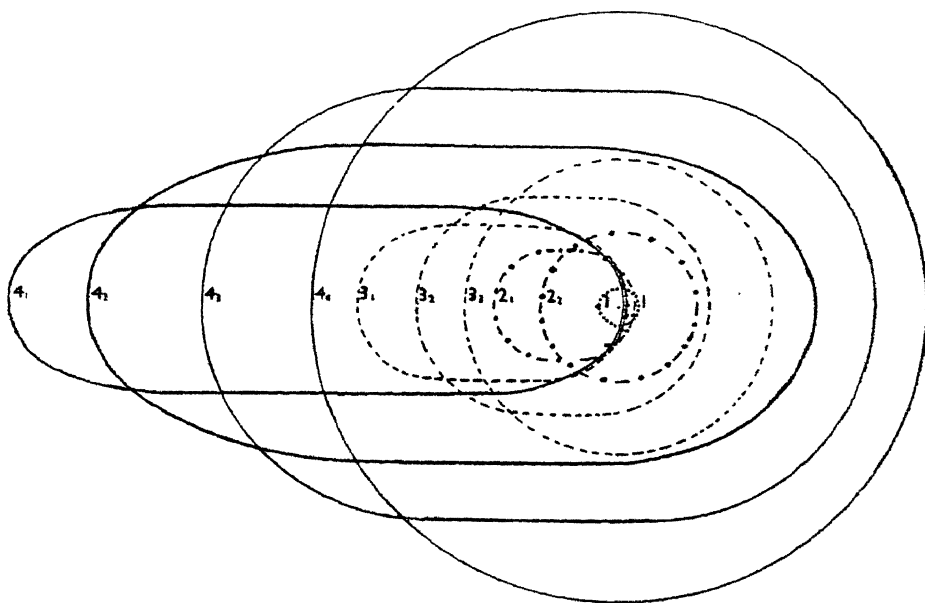


FIG. 3.

Each sheath or set of orbits is marked distinctly but the diagrams are not intended to give any information relating to the relative sizes of the different sets of orbits or sheaths. From theoretical considerations, it has been found, however, that the outermost sheath for any uncombined atom, however complex it may be, cannot contain more than eight electrons, generally referred to as an "octet," and the sheath which is next to the outermost not more than eighteen. When an atom is in a state of combination the outer sheath may, however, contain 8, 12 or even 16 electrons, the larger sheaths being found with the heavier elements.

THE DEVELOPMENT OF THE VARIOUS ORBITS FROM  $1_1$  TO  $4_1$ .



G. 4.

Oxygen has two sheaths of electrons with two in the first sheath and six in the outermost. Chlorine has three sheaths containing respectively two, eight and seven electrons, whilst chromium has four sheaths. In chromates the four sheaths of the chromium atom are considered to contain two, eight, eight and six electrons respectively. In chromic salts the suggested arrangement of the unionised chromium atom is two, eight, eleven, three, and in chromous salts, two, eight, twelve, two. The electrons in the outermost set of orbits are considered to be the valency electrons and their number determines the valency of the element in question. Sidgwick (1927) gives the following electronic structure for the chromium atom: two, eight, twelve, two, or, more probably, two, eight, thirteen, one. Sidgwick points out that there is no reason to think that any increase in the fourth sheath beyond two takes place until the third sheath is completed (with eighteen

electrons). The most recent information concerning the electronic structure of the chromium atom gives the arrangements of the electrons in the sheaths to be two, eight, twelve, two (Morgan, 1938).

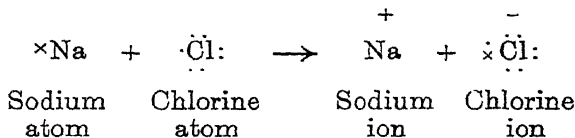
Now the inert gases of the atmosphere, helium, neon, argon, etc., are assumed, because of their lack of combination with any other element, to represent the most stable arrangement of the electrons in their sheaths and this is attributed to the fact that their outermost electronic sheaths are completed. That is to say, the first electronic sheath is complete when it contains two electrons (helium contains two electrons); the second when it contains eight electrons (neon contains two and eight electrons in its two sheaths). The third sheath is also complete with eight electrons (argon has two, eight, eight electrons). Krypton, the next inert gas, has two, eight, eighteen, eight electrons and so on. The sheaths attain a state of comparative stability when they have eight or even eighteen electrons, even if they are capable of holding eighteen or thirty-two.

Atoms other than those of the inert gases contain in their outermost sheaths one or more electrons which are relatively loosely held and are affected in ordinary chemical reactions, the rest of the atom remaining unchanged. Such atoms in chemical combination try to attain to an inert gas structure, as it is called, and thereby attain a condition of stability or inertness. Electronegative elements, such as chlorine, oxygen and non-metals in general, tend to take up electrons, whereas electro-positive elements, such as sodium and metals in general, tend to give up electrons. Thus the neutral atom of oxygen  $\ddot{O}$ : with six electrons in the second or outermost sheath will tend to gain *two* electrons, each of which is equivalent to one unit charge of negative electricity and so form a *bivalent* negative oxygen ion  $\times\ddot{O}:^-$ . This addition of electrons brings the number in the outermost sheath up to eight and thereby completes the octet. Chlorine  $\cdot\ddot{Cl}$ : with seven electrons in the outermost sheath would try to gain *one* electron and so form a *monovalent* negative chlorine ion  $\times\ddot{Cl}:^-$ ; sodium  $\times Na$  with *one* electron in the outermost sheath and eight in the next lower sheath would tend to lose one electron and form a positive *monovalent* ion, whilst calcium  $Ca^\times$  with two electrons in the outer sheath and eight in the next lower sheath would tend to lose *two*. Valency can thus be defined electronically as the number of electrons an atom must lose, if electropositive, or gain, if electronegative, to have a total number capable of forming a stable arrangement, the actual number of electrons in the ion so formed tending to be that of the nearest inert gas. This does not involve the acceptance of any particular atomic model but only assumes that some of the electrons are firmly held and unaffected by external influences whilst there are others which are active in chemical combination.

Chemical combination can, therefore, be pictured as the tendency of the electrons to re-distribute themselves among the atoms involved so as to form more stable arrangements, such as

occur in the inert gases. Chemical combinations or linkages may be divided into three types: (1) polar or ionisable linkages between the oppositely charged ions of a salt; (2) non-polar, non-ionisable linkages, such as are especially found in organic compounds; (3) the co-ordinate linkages of Werner, which are capable of linking apparently saturated molecules.

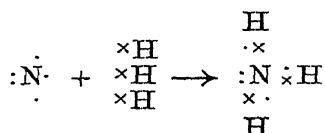
The characteristics of the first type, known as electro-valent linkage, may be illustrated by the combination of, say, a sodium atom  $\times\text{Na}$  and a chlorine atom  $\cdot\ddot{\text{Cl}}:$ . The sodium atom gives up one electron to the chlorine atom and the chlorine atom takes up this electron and thereby both atoms obtain octets. The sodium atom, by giving up an electron, that is a unit negative charge, becomes the unit positively charged sodium ion  $\overset{+}{\text{Na}}$ , whereas the chlorine atom, by accepting a unit negative charge (an electron), becomes the chlorine ion with one negative charge,  $\ddot{\text{Cl}}:$ . The two ions are held together by electrostatic charges only and are not held by directional bonds.



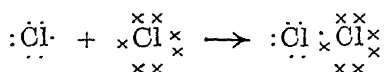
This type of linkage is found, in general, when an electropositive element or radicle unites with an electronegative element or radicle and an electrolyte results, the linkage being electro-valent. The combination of the chromium atom with three chlorine atoms to give chromium trichloride is the same type of change. The chromium atom gives up three electrons, one to each of the chlorine atoms. Thus the chromium atom becomes the chromium ion and is represented by  $\text{Cr}^{+++}$ , carrying three positive charges, and the chlorine atoms become the negatively charged chlorine ions. In compounds of this type (type 1 of the Werner series) ionisation occurs into one positively charged chromium ion and three negatively charged monovalent ions or their equivalent. The case of chromium is not, however, so simple as that of sodium and calcium given above, for after losing the 3 valency electrons, the chromium ion is left with eleven electrons in its outer sheath, an unstable number. This number has to be made up to a stable configuration. The method of doing this is dealt with below.

The second type of valency linkage is what is known as a co-valent linkage. A co-valent linkage results when electrons are shared between two atoms so that each shared electron enters into the constitution and contributes towards the stability of both atoms. The elements involved are generally, although not always, electronegative and the resulting compounds are not ionisable. This sharing of electrons can only occur in pairs and the pair of electrons shared between two atoms is the ordinary valency bond. For example, the atom of nitrogen which has 5 electrons in its outer orbit can take up three electrons and the hydrogen atom can take up one electron. As shown below, each of three hydrogen atoms gives one electron and the nitrogen atom three electrons

towards the sharing of three pairs by which the nitrogen atom has gained its three electrons, completing its octet, and the hydrogen atoms have each received an additional electron, thereby attaining an inert gas structure.

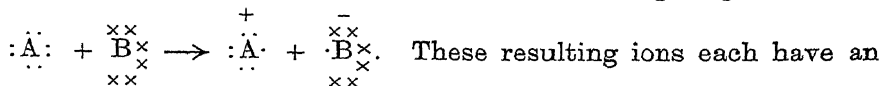


Similarly, the chlorine atom can share an electron with another chlorine atom, each atom of the pair becoming satisfied, as shown below. This is what occurs in the common gases, two atoms being linked co-valently to form a molecule.



The presence of a covalent link, as this type of linkage is called, implies a definite directional bond, which is non-ionised. Stereo-isomerism thus becomes possible. This type of isomerism never occurs in purely electrovalent compounds since the union in such cases is non-directional and merely depends on a general electrostatic attraction. As already described, stereo-isomerism has been observed in compounds such as chromium compounds containing an electrovalency but it is the covalencies in the molecule which are responsible. The number of covalent links cannot exceed the number of electrons which an atom has to offer.

A third type of valency linkage which is met with very frequently in chromium salts, for example, can be regarded as a combination of electro-valency and covalency. This mixed type is known as co-ordinate valency and the linkage as a co-ordinate link. It is directional and non-ionised by virtue of the covalency part of its linkage and as a consequence of the electrovalency part the atoms or radicles taking part become positively and negatively charged respectively. Thus a compound containing a co-ordinate valency will be "polar," that is, the molecule as a whole is neutral, but the centres of gravity of the positive and negative charges do not coincide. It will be remembered that in a covalent link the shared electrons were provided by each of the elements concerned in the linkage. In a co-ordinate link, however, the electrons which are to be shared are provided by only one of the atoms concerned. The atom providing the electrons, of which there must be a pair, is known as the "donor" and the process as "donating." The atom receiving the electrons is known as the "acceptor." The co-ordinate valency can be regarded as made up as shown in the following example. The two atoms involved are A (the donor) and B (the acceptor). It may be imagined that an electron is first donated from A to B, this giving  $\overset{+}{\text{A}}$  and  $\overset{-}{\text{B}}$ .



unpaired or a " lone " electron and can acquire greater stability by sharing this with the other in a covalent bond,

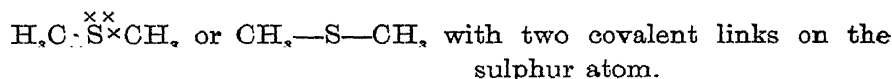


The resulting linkage is a co-ordinate

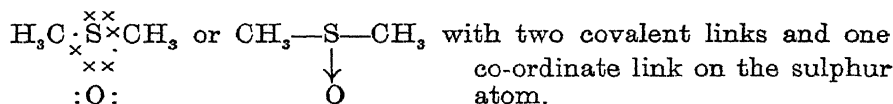
linkage and it has just been shown to be a combination of one electrovalency and one covalency. The linkage may be represented as  $\overset{+}{A}-\overset{-}{B}$  or  $A \rightarrow B$  or  $A \longrightarrow B$ , the head of the arrow pointing in the direction in which the pair of electrons has been transferred, thereby denoting the method by which the link has been formed.

In some instances, both the " donor " and " acceptor " are capable of independent existence and the co-ordinate link is fairly readily broken. When broken, the previously shared pair of electrons returns to its former position. In other cases, however, it forms a link which is as strong as a covalent link. The " donor " does not change the number of its outermost electrons, whereas the " acceptor " increases its own number by two for every co-ordinate link. The following are some illustrations of covalent, co-ordinate and electrovalent linkages.

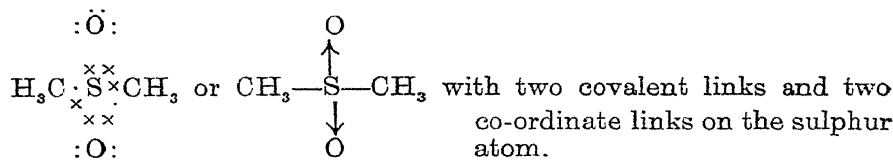
Dimethyl sulphide



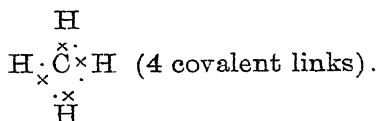
Dimethyl sulphoxide



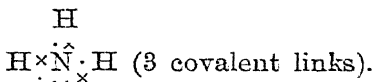
Dimethyl sulphone



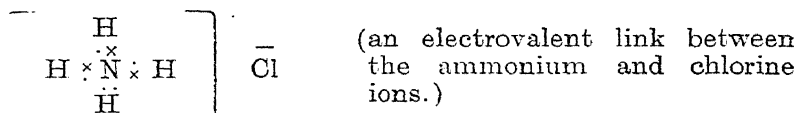
Methane



Ammonia



Ammonium chloride



Water



The water molecule is particularly interesting, it can co-ordinate in two ways. It can accept electrons on the hydrogen atom,  $X \rightarrow H-O-H$ , or can donate electrons from the oxygen atoms,

$X \leftarrow O \begin{matrix} \nearrow H \\ \searrow H \end{matrix}$ ; which might be termed a two-edged effect. This is

probably the cause underlying the great tendency of water molecules to associate with other molecules and form co-ordinate linkages. The second form of linkage occurs more readily than the first. An atom is more likely to act as a donor when it is negatively charged and an acceptor when positively charged. Kations act as acceptors and form co-ordinate links with the oxygen of the water while anions attach to the hydrogen.

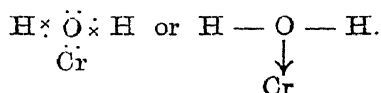
The view that electrovalency and co-ordination valency are essentially distinct states of linkage is supported by the fact that the co-ordination number of an element remains constant in a series of compounds in which the electrovalency of a co-ordinated complex varies within wide limits and even changes sign according to the nature of the co-ordinately linked groups.

A shared electron counts as one towards the stable electron number for each atom. Both the nuclei are within the orbit which is, however, of the same general kind as those of the unshared electrons of that nucleus. An octet is an extremely stable group of electrons, not only when it is unshared, as in the inert gases, but also when it is completely shared (as in four covalent linkages to one atom) or when built up by covalent and co-ordinate linkages.

### (iii) THE CONSTITUTION OF VARIOUS CHROMIUM COMPOUNDS DISCUSSED IN THE LIGHT OF THE WERNER CO-ORDINATION THEORY OF VALENCY AND THE ELECTRONIC THEORY OF VALENCY.

The electrovalent link between the chromium ion and three chlorine ions is not, according to the Werner concept, the whole story as far as the chromium atom is concerned, nor, indeed, is it the whole story according to the electronic theory, since the chromium atom having lost 3 valency electrons is left with an unstable configuration in what has now become the outmost sheath. In the Werner theory of valency, the chromium is depicted as co-ordinately linked with six water molecules to form a complex ion with three positive charges. According to the electronic theory it has given up three electrons to three chlorine atoms, forming three chlorine ions, as in chromium trichloride, acquiring in this way three positive charges. The chromium ion in the solution of say, chromium trichloride consists of a complex ion containing six molecules of water  $[(H_2O)_6.Cr]^{+++}$ . The atom of chromium can form six co-ordinated valencies instead of the four found in lighter elements and so can build an outermost sheath of twelve shared electrons which, round certain large atoms, can form a stable state. It can further be shown that each of the six water molecules mentioned above is linked to the central chromium atom by means of a co-ordinate valency, the

oxygen atom of the water molecule providing both shared electrons to form a co-ordinate link with the chromium atom. This can be illustrated for one molecule of water as follows, the other five being exactly similar:—



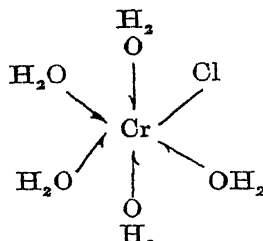
This implies that, and explains why, the water molecules are not present as solvent and any groups replacing them in the chromium complex are not individually ionised but form part of a complex chromium ion. By virtue of the covalent part of the co-ordinate linkage the valency bonds between water molecules or similar groups and the central chromium atom are directional. This is in harmony with Werner's explanation of stereo-isomers in chromium compounds. Furthermore, the co-ordinate linkage between the six water molecules or similar neutral molecules and the central chromium atom does not involve any alteration to the nett electrical charge on the chromium complex and, therefore, the complex chromium ion retains its three positive charges.

The chromium atom belongs to the group of atoms which have their outermost and next outermost electronic sheaths imperfectly filled—the number of electrons in the completed sheaths being 8 and 18 respectively. The valency group of electrons is not fixed in this type of atom as one or more electrons from the next incomplete group may be utilised for chemical combination. Thus, according to Sidgwick (1927), the chromous ion  $\text{Cr}^{++}$  has an electronic structure represented by two, eight, twelve, with a group of twelve electrons in the third sheath, although by chemical action, a third electron is readily removed, giving the chromic ion  $\text{Cr}^{+++}$  with a two, eight, eleven arrangement. It has already been mentioned that this is an unstable configuration and the chromium ion with its positive charges forms an outer sheath of twelve electrons by co-ordinating with six water molecules. The addition to the chromium ion of six molecules of water, which are co-ordinately linked, allows the chromium ion to enter into the sharing of twelve electrons (sharing six pairs of electrons associated with the six oxygen atoms in the six water molecules), thus adding twelve electrons to the above arrangement and attaining the stable configuration two, eight, eleven, twelve.

It is next proposed to consider what happens when one of the neutral water molecules is replaced by a chlorine ion or an OH ion. According to Werner, such replacement involves at least two fundamental changes. Firstly, the Cl or OH in the complex is no longer ionised as such, but forms part of a complex chromium ion. Secondly, the entrance of the Cl ion or OH ion into the complex displaces a molecule of water and reduces the nett electropositive charge of the complex chromium ion from 3 to 2. It can be seen

from the electronic structure of the chlorine ion  $:\ddot{\text{Cl}}:$  that it resembles the water molecule in having more than one pair of unshared or lone electrons, and can, therefore, form co-ordinate

links. The link between the chromium atom and the chlorine atom is represented differently from the case of water, for example:—



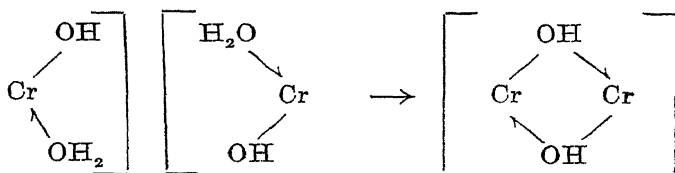
The difference in the manner of representing these linkages is not intended to imply that their method of formation has been different. In this report, co-ordinate linkages which are formed by the entrance of neutral groups into the chromium complex and which do not affect the nett charge on the complex will be represented by  $\rightarrow$ , but where the entering group is an anion, such as OH, Cl,  $\text{SO}_4$ , etc., which affects the nett charge on the chromium complex in changing from ion to atom, the link will be represented by  $\dashv$ .

The chlorine atom, being co-ordinately linked to the chromium atom, is not ionised and in passing from ion to atom has given up its unit negative charge to the chromium complex thereby reducing the nett positive charge on the complex by one unit. Thus the electronic theory explains satisfactorily the requirements outlined above. The case for the introduction of an OH group into the complex in place of a chlorine atom can be represented in a very similar manner, the electronic arrangements being parallel. For example, the chlorine atom is  $\text{:}\ddot{\text{Cl}}\text{:}$  and the OH group  $\text{:}\ddot{\text{O}}\text{:}$ , and the chlorine ion is  $\text{:}\ddot{\text{Cl}}\text{:}$  and the OH ion  $\text{:}\ddot{\text{O}}\text{:}$ .

The OH ion gives rise to a co-ordinate link in the same way as described above for the chlorine ion. The linkage may be represented,  $\text{Cr}-\text{OH}$  and can be referred to as a single co-ordination linkage (see below). This is the process which occurs when a normal chromium salt is dissolved in water and hydrolyses, or when a chrome liquor is made basic.

The reverse occurs when acid is added to a basic solution of a chromium salt. The hydrogen ions in the solution of acid link up with the OH groups inside the complex forming  $\text{H}_2\text{O}$ , which is in co-ordinate linkage with the chromium atom.

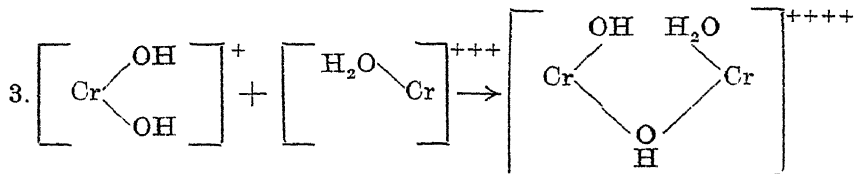
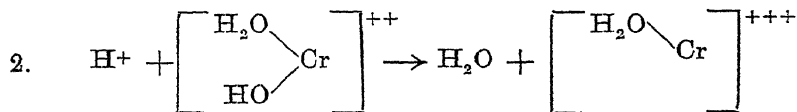
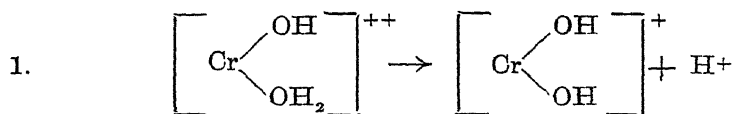
As described above, Stiasny pays considerable attention to a process which he calls "verolung" (olation), and which is represented on the Werner concept as follows:—



## THE CHROME TANNING

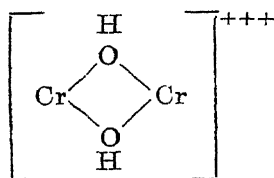
The oxygen atom of the olated OH groups, it will be noticed, is now linked by two co-ordinate links to two chromium atoms. The nett electric charge on the chromium complex per atom of chromium has not altered as a result of the olation process. According to Stiasny, the olated OH groups are linked by a principal valency to one chromium atom and an auxiliary valency to a second, that is the two linkages are different. This linkage may be described as a double co-ordinate linkage. According to Stiasny, the process of olation can lead to the formation of compounds of high molecular weight. The configurations suggested by Stiasny for this type of compound consist of chains of chromium atoms linked by olated hydroxo groups. From what has been said, the formation of these can easily be followed.

Olation may be represented, according to the electronic theory, as follows:—The oxygen atom of a water molecule inside the chromium complex has, by the process of co-ordination, acquired a positive charge, and this charge, coupled with the positive field of the kationic complex, may cause a hydrogen ion to be detached from the oxygen of the water molecule. Since hydroxo groups are titratable with acid, the hydrogen ion will react with and remove a hydroxyl group from a second complex. The outer sheath of the chromium atom in the second complex now contains ten electrons, and is made up to the stable configuration of twelve electrons by the formation of a co-ordinate link with the oxygen atom from which the hydrogen atom was originally detached. The nett result of this process is the formation of a complex which contains two chromium atoms, with loss of one molecule of water and no change in the total number of positive charges associated with the two chromium atoms.

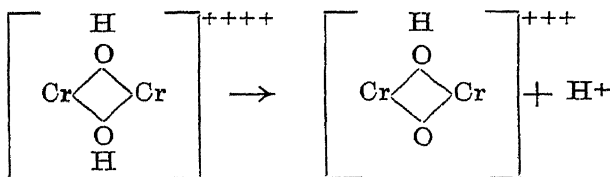


In the same way, a hydrogen ion may be detached from a water molecule in the second chromium complex. If, in the first complex, a hydroxo group was in *cis* position to the reacting aquo

group, water may again be eliminated, and a diol linkage formed, giving a complex of the type:—



If no such *cis* hydroxo group was present, Ol formation may take place with a third chromium complex, and by continued reaction in this way compounds of high molecular weight, containing chains of chromium atoms linked by olated hydroxo groups, may be formed. Finally, if no further aquo groups are present to react with the hydrogen ions, the liberation of these ions will bring about the increase in acidity on standing which is characteristic of basic chrome liquors. This increase in acidity may also be brought about by the loss of hydrogen ions from the OH groups of the Ol link. The well known instability of oxonium compounds shows that such loss of a positively charged group from triply-linked oxygen is usual. The result of this last reaction will be the formation, in place of an Ol link, of a link composed of a divalent oxygen atom, and the loss of one positive charge from the complex.



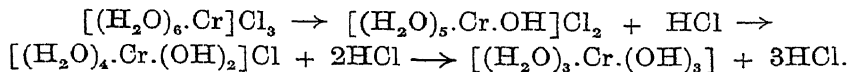
The formation of such divalent oxygen bridges has been described by Stiasny (1931). Werner gave the name of " $\mu$  oxo" compounds to the products of this change.

#### (iv) THE ACTION OF WATER AND ALKALIES UPON CHROMIUM SALTS.

##### (a) *Hydrolysis Effects.*

In the production of chrome leather, the chromium salts are used dissolved in water. The behaviour and properties of aqueous solutions of chromium salts is very largely dependent upon hydrolytic processes and processes secondary to these. A consideration of these changes is very necessary for an understanding of the tanning action of chrome liquors.

According to Werner and Pfeiffer (1923), the hydrolysis of chromium salts can be regarded as the splitting off of hydrogen from the  $\text{H}_2\text{O}$  groups of the complex, for example,



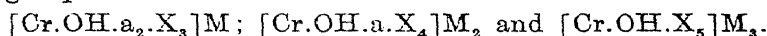
This is fundamentally the same change as occurs in olation (see below). The hydrolysis of chromium salts is always associated with the formation of acid and the process may be accelerated by

the addition of alkali or retarded by the addition of acid. This setting free of acid is met with when "blues" are horsed up for a time after tanning. The acid is removed in the neutralising process by the use of alkalies such as borax. From the above, it would seem that if the chromium complex contains no  $H_2O$  groups, then no hydrolysis will occur and this may be a possible explanation as to why some chrome blues do not become acid when horsed up, *i.e.*, that the chromium collagen compound no longer contains an  $H_2O$  group associated with the chromium atom and does not hydrolyse further.\*

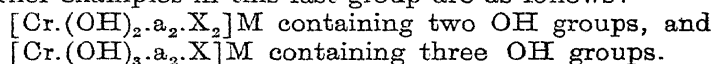
In addition to setting free acid, hydrolysis leads to the formation of what are known as basic chromium salts and as these are of great importance in chrome tanning, they will be considered next. The first possibility that the hydroxyl group may be combined by an electrovalent linkage, *i.e.*, outside the complex, can, according to Stiasny, be dismissed at once as such salts are extremely rare and, furthermore, the aqueous solution of the chromium salt would react alkaline. This leaves the alternative that the OH groups are within the complex, forming hydroxo compounds. The following possibilities may be considered: (1) that the complex chromium ion is positively charged or (2) that it is not charged at all, and (3) that the complex chromium ion is negatively charged. The following are examples of the first two possibilities:—

- (1)  $[Cr.OH.a_5.X_2]$  and  $[Cr.OH.a_4.X]X$  which are 33 per cent. basic and  $[Cr.(OH)_2.a_4]X$  which is 66·7 per cent. basic.
- (2)  $[Cr.OH.a_3.X_2]$  which is 33 per cent. basic and  $[Cr.(OH)_2.a_3.X]$  which is 66·7 per cent. basic.

From a tanning aspect, all of these compounds are of the greatest importance. The following are examples of the third possibility, with anionic chromium complexes and containing one OH group:—

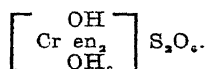


Further examples in this last group are as follows:—



The impression that salts containing negative chromium complexes do not tan is not correct, as there are a number of valuable chrome tanning liquors which contain anionic hydroxo chrome complexes (Stiasny, 1931). The difference between kationic (positively charged) complexes and anionic (negatively charged) complexes is demonstrated by what happens on the addition of alkali. In the former case, an addition of alkali lessens the positive charge on the complex, lessens the solubility of the chrome salt and, from a tanning standpoint, the chrome salt becomes more and more astringent. In the latter case, the addition of alkali in-

\* Stiasny (private communication) points out that there are chromium compounds which do not hydrolyse and consequently react neutral in aqueous solution although they contain aquo groups in the chromium complex, *e.g.*:

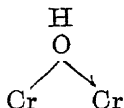


creases the negative charge on the anionic complex and from a tanning aspect the chrome salt becomes less and less astringent.

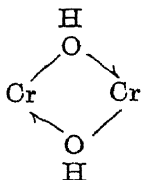
A further class of hydroxo compounds which has been described earlier is that of the Ol compounds. This class will next be considered in even greater detail.

(b) *Olation*.

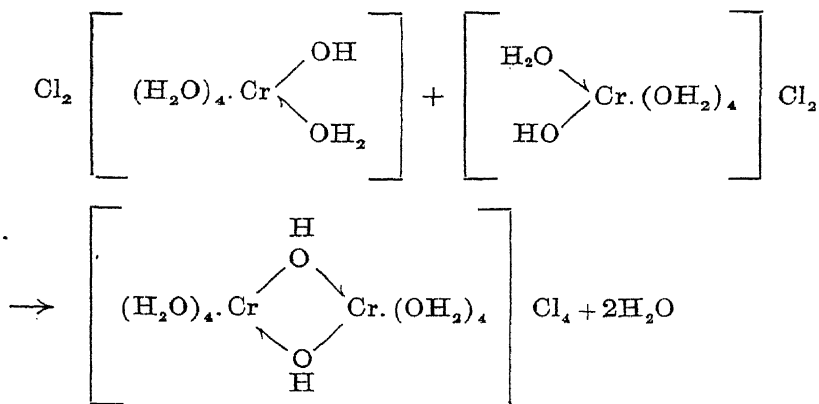
It has already been pointed out that Ol compounds are characterised by hydroxyl groups which are co-ordinately linked to two chromium atoms. The typical linkage can be represented as follows:—



The number of such Ol groupings, as they are called, is incorporated in the name of the chromium salt in question, for example, a "diol" compound would contain two such groups,



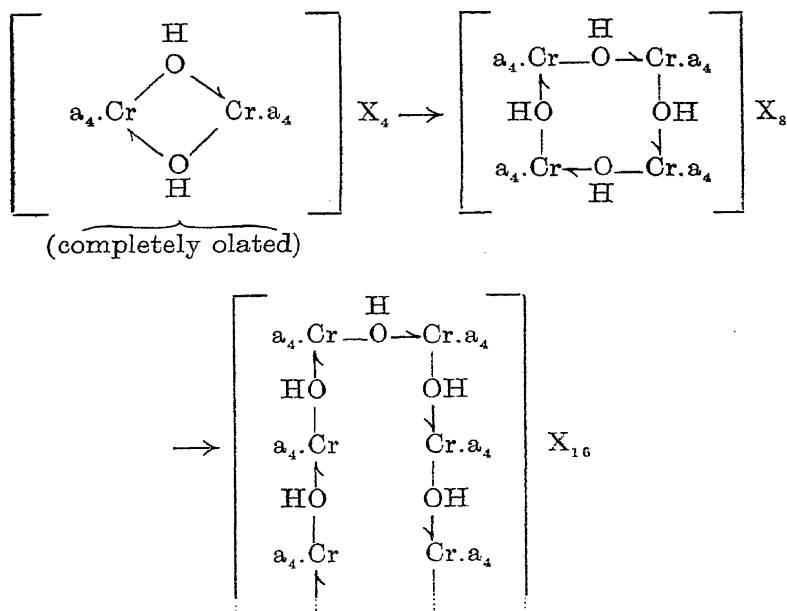
and so on. An example of such a diol compound and its formation is given earlier. Pfeiffer has isolated a diol chromium compound (the diol-tetraen-chromi-dithionate) and proved the mechanism of its formation. In quite an analogous way Ol compounds can form or be formed from ordinary basic chromium salts (hydroxo salts). These compounds are of the greatest importance in tanning and will be considered further. For example, basic chromium chloride solutions which have been heated or allowed to stand may, with certainty, be considered to contain such compounds (Stiasny, 1931), the formation of which takes place as follows:—



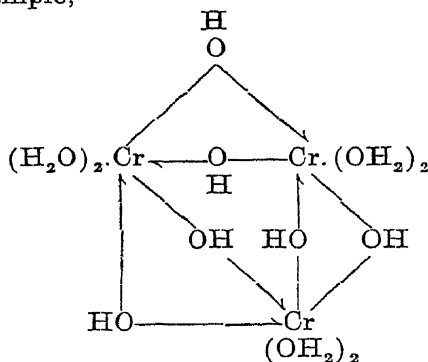
In a similar manner, more complicated olated compounds can arise, particularly from more basic solutions, for example, six mole-

cules of the 66.7 per cent. basic chloride,  $[(H_2O)_4.Cr.(OH)_2]Cl$ , can give rise by olation to a chromium salt containing six diol groupings. According to Stiasny (1931), this strongly olated compound forms a semi-colloidal solution. With an increasing degree of olation the size of the molecules increases and the solution approaches nearer and nearer the colloidal condition. This, according to Stiasny is essential from a tanning standpoint since particles of an intermediate size are necessary to give a chrome liquor which will tan. Too small particles have no tanning properties and too large particles are unable to penetrate the collagen fibre. Olation converts a chromium solution into the semi-colloidal or colloidal condition. Bjerrum (1907, 1910, 1924) did not give constitutional formulæ to such olated compounds in order to distinguish them from hydroxo compounds. He based his conclusions as to the formation of these latent basic salts, as he called them (that is salts which do not interact readily with hydrochloric acid), upon the titration curve of a chromium chloride solution with sodium hydroxide. Back titration with hydrochloric acid gave a curve which did not coincide with the first curve.

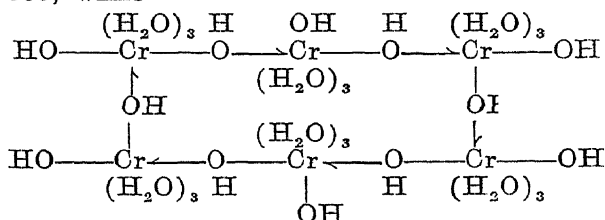
It can be shown how by olation a 33 per cent. basic chromium chloride solution, on heating or ageing, can give rise to a compound of a molecular weight of 282 and a 66.7 per cent. basic chromium chloride solution, to a compound of molecular weight 732. In a similar manner, it can be shown that basic chromium chloride solutions of still higher basicity, *i.e.*, 83 per cent., can give Ol compounds of molecular weight 1350. The molecular size of a basic chromium salt is, however, not limited by the basicity and the degree of olation. A basic chromium salt, which is completely olated, can still increase in molecular size by polymerisation on further heating its solution, as shown in the following general example:—



Olation and polymerisation proceed, in a way, on parallel lines as they are affected by the same factors, *i.e.*, increase in basicity, ageing, temperature. The two processes are, however, different. Olation is a condensation process in which water is eliminated and an increase in molecular size occurs. In the other process, simple Ol compounds join up together, that is, polymerisation occurs. With chromium salts containing more than one chromium atom in the complex, it is extremely important to distinguish between olation and polymerisation. The degree of olation is the proportion of Ol groups to the total number of hydroxyl groups. A complex can be 100 per cent. olated and of low molecular weight, whilst another might be 50 per cent. olated and of high molecular weight. For example,

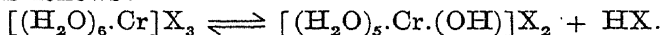


is 66.7 per cent. basic, 100 per cent. olated and has a molecular weight of 366, while

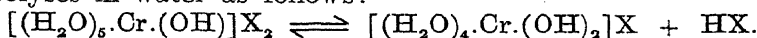


is 66.7 per cent. basic, 50 per cent. olated, and has a molecular weight of 846.

An important feature which accompanies the process of olation of all basic chromium salts is the increase in acidity of the solution. When a chromium salt is dissolved in water, hydrolysis occurs as follows:—



The basic salt so formed olates, giving  $[(\text{H}_2\text{O})_4.\text{Cr}(\text{OH})]_2\text{X}_4$ . This disturbs the hydrolysis equilibrium shown above by removing hydroxo salt and further hydrolysis occurs with the setting free of more acid, thereby increasing the free acidity of the solution. These changes, which proceed slowly, occur much more quickly on heating. Basic chrome liquors become more acid on standing. For example, the 33 per cent. basic chrome liquor produced from a normal chromium salt by the addition of sodium hydroxide hydrolyses in water as follows:—



Olation of the basic hydrolysis product disturbs the hydrolysis equilibrium and more hydrolysis occurs. Thus, if a chrome liquor is made basic, then on standing the acidity of the liquor slowly increases, partly due to hydrolysis and partly to olation (Stiasny, 1931). An alternative explanation of the increase in the acidity of basic liquors on standing is given above in terms of the electronic theory.

Attention has already been drawn to the fact that hydroxo compounds interact immediately with acids such as HCl. On the other hand, olated basic salts (Ol compounds) are relatively stable to acids (interaction is slow). If dilute hydrochloric acid is added to an Ol compound then interaction only occurs very slowly but may be hastened by the use of a stronger solution of acid or by heating, the complex being thereby split up. The action is the exact reverse of olation. According to Stiasny (1931) the Ol linkage is not the same in its resistance to acids for all such compounds but is influenced in this respect by the other groups in the complex. The order of increasing resistance of the Ol linkage towards the action of acids as affected by other groups in the complex is as follows: tartrate—oxalate—formate—acetate—sulphate—chloride—nitrate, that is the reverse of the order giving the penetration power of these anions into the chromium nucleus (nitrate has the least and tartrate the greatest power of penetration). This is also the order in which these groups are held within the complex, starting with the group most strongly held and ending with that least strongly held. Thus the Ol linkage is most easily broken where the remaining groups are most *strongly* held within the complex.

Using the method outlined earlier in Chapter V for the determination of the degree of olation, Stiasny and Königfeld (1932) have studied the influence of concentration, basicity, temperature and additions of neutral salts upon the degree of olation and the velocity of formation, of Ol compounds from basic chromium chloride and sulphate solutions. These basic chrome liquors were found to be extensively olated. The olation change commences even during the operation of making the liquor basic and after a rapid progress in the first five hours, continues steadily. Eventually, after several weeks of such progress, it approaches to a limiting value which is dependent upon the concentration, basicity and temperature of the chrome liquor. Freshly prepared and slightly aged liquors are in a state of steady change. Liquors aged for some time (more than one or two weeks) do not alter much further. Their use offers, therefore, greater safety to the practical tanner. Chromium sulphate liquors olate more quickly and to a greater extent than chromium chloride liquors of comparable concentration and basicity. Chrome liquors, which at higher temperatures are extensively olated, gradually become less olated on allowing them to age at lower temperatures and after a few weeks approach the same degree of olation to which they would have attained by ageing without heating. The process of olation is thus reversible.

Complex chromium salts containing  $\text{CO}_3$  within the complex which arise when sodium carbonate is used for making chrome liquors basic, have a retarding effect on the olation of chromium

chloride and chromium sulphate liquors. During several weeks' ageing,  $\text{CO}_2$  is gradually evolved from the complex and the difference in the degree of olation of liquors rendered basic with sodium carbonate and sodium hydroxide respectively, disappears.

Additions of sodium chloride do not affect the degree or the rate of olation whether added to chromium chloride or chromium sulphate liquors and whether added before or after the liquors were rendered basic.

Additions of sodium sulphate assist the process of olation if the addition is allowed to act for at least several days so that noticeable amounts of  $\text{SO}_4$  groups can penetrate the chromium complex.

The degree of olation increases with increasing concentration of chromium, is rapid in the first five hours even in dilute solutions (up to 1 per cent. chromium), is greater the greater the basicity and the values after four weeks are greatest in the most basic liquors. The degree of olation increases rapidly with a rise in temperature and after any period of time reaches the highest value at the highest temperature. The longer a basic solution is maintained at a definite temperature, the greater is the degree of olation.

#### (c) *Molecular Size and Colloidal Nature.*

It is suggested earlier in this chapter that there may be some relation between the size of the chromium complex and the degree of olation and polymerisation of chromium salt solutions.

Stiasny and Grimm (1927) dialysed chromium salt solutions in order to determine roughly the extent of increase in particle size upon olation and found that 97 per cent. of the hexaquo chromium chloride passed through a parchment thimble. Boiling this solution for sixty hours, cooling and dialysing immediately, reduced this percentage to 94. For pentaquo-hydroxo-chromi-chloride basicity = 33 per cent., the value was 87 per cent., and this was not altered by boiling for five minutes and cooling. Thus in these tests olation did not result in the formation of very large complexes. By intermittent additions of sodium hydroxide to a solution of hexaquo-chromi-trichloride until a basicity of 86–90 per cent. was reached, a solution was obtained which gave a slight Tyndall cone. On dialysis, only 0.5–2.0 per cent. of the chromium salt present passed through a parchment membrane, thus indicating that a high degree of molecular complexity had been attained.

F. L. Seymour Jones (1923) showed that basic chromic sulphate solutions, such as are used in tanning, may contain no colloidal matter and still be capable of tanning. The solutions used passed unchanged through a collodion ultra-filter.

Jander and Scheele (1932) investigated the condition of aggregation in solutions of salts of tri-valent metals, in particular in aqueous chrome salt solutions. Alterations in the average molecular weight of the basic chromium nitrates formed by the addition of sodium hydroxide to chromium nitrate solutions were followed by means of changes in the diffusion coefficients of the solution. In solutions of a pH value of 3.0 and less the diffusion co-efficient altered only slightly. From pH = 3.0 (33 per cent. basic salt) upwards the diffusibility decreased rapidly. The molecular weights of the chromium salts in solution were calculated

from their diffusibility. The results are given in tabular form below. The molecular weight for the 33 per cent. basic salt was 440, for the 67 per cent. basic, 1750, and for the highly basic soluble chromium compound obtained on adding 2.35 molecules of sodium hydroxide per 1 atom of chromium was 84,000. The composition of the salts present was calculated, and it was found that bimolecular salts were prominent at 33 per cent. basicity, *i.e.*, with two chromium atoms per molecule; at 67 per cent. basicity the molecules contained an average of 13 chromium atoms in the complex, whereas in the highest basic solution the chromium complexes contained 600—700 chromium atoms.

TABLE V.  
THE MOLECULAR WEIGHTS OF BASIC CHROMIUM NITRATES.

Percent- age basicity.	Mol. NaOH added per 1 Cr.	Immediate pH value.	Equilibrium pH value.	Diffusion coeffi- cient.	Average molecular weight.	No. of Cr. atoms per molecule.
0	0	—	—	0.31	284	1
	0.235	3.53	2.73	0.29	325	1.1
	0.469	3.93	2.88	0.28	348	1.2
	0.703	4.24	2.99	0.28	348	1.2
	0.938	4.72	3.10	0.26	404	1.4
33.3	1.000*	—	—	0.25*	440	1.6
	1.17	4.76	3.18	0.23	516	2.5
	1.41	4.79	3.32	0.23	516	2.5
	1.64	5.03	3.40	0.16	1090	5.4
	1.88	5.23	3.51	0.15	1210	6.0
66.7	2.00*	—	—	0.125*	1750	9—13
	2.11	5.24	3.67	0.09	3370	26
	2.35	5.34	4.10	0.018	84000	650

\* Interpolated.

Riess and Barth (1935) have also used diffusion methods for determining the molecular weight of the chromium compounds in various chromium salt solutions. The solutions were prepared from the corresponding hexaquo salts, sodium hydroxide being used in the preparation of liquors of various basicities. The liquors so prepared were allowed to age for several weeks until no further changes in their pH values occurred. The following table gives the molecular weights obtained by these authors. In every case the solution under examination contained 0.7 per cent. chromium.

TABLE VI.  
THE MOLECULAR WEIGHTS OF BASIC CHROMIUM NITRATES, CHLORIDES  
AND SULPHATES.

Percent- age basicity.	Molecular Weight.			Chromium atoms/molecule.		
	Nitrate.	Chloride.	Sulphate.	Nitrate.	Chloride.	Sulphate.
0	346	267	608	1	1	2
33.3	442	484	796	1.7	2.3	3.7
50	758	737	947	3.4	4.0	5.2
54	—	—	1906	—	—	11.0
59.5	1190	1320	—	5.9	7.8	—
66.6	4080	1700	—	22.1	10.8	—

The heating of solutions of chromium chloride (0.7 per cent Cr) for one hour had practically no effect on the molecular size in 33.3 per cent. up to 66.6 per cent. basic solutions, but with 0 per cent. basic there was a moderate increase in the molecular weight.

The addition of masking substances, namely, sodium formate up to an addition of 2 molecules formate per 1 Cr, and sodium oxalate, had practically no effect on molecular size for chromium nitrate liquors (0—33.3 per cent. basic). Furthermore, the addition of sodium sulphite (0.5 mol. per 1 Cr) to a chrome alum solution brought about a considerable immediate increase in the molecular size which diminished gradually on standing.

The theoretical significance of these experiments will be dealt with in Chapter VII.

#### (v) THE DISPLACEMENT OF WATER MOLECULES FROM THE CHROMIUM COMPLEX.

It has been shown above how the water molecules in the chromium complex in, say, hexaquo-chromi-trichloride can be displaced by OH. The water molecules may also be displaced from the chromium complex by various anions, such as Cl,  $\text{SO}_4$ . When a divalent anion penetrates the complex, it usually displaces two of the water groups from the complex.

The various anions differ very widely in their ability to penetrate into the complex, displacing water groups. The penetrating power for the nitrate ion must be very low; the only normal chromic nitrate known is the hexaquo salt with no nitrate ions present in the complex. Chlorides show some tendency to penetrate into the complex, but not nearly so much as sulphates and hydroxides. Oxalate and tartrate ions enter the complex with great ease. The power of penetration of anions into the chromium complex increases in the order: nitrate, chloride, sulphate, formate, acetate, oxalate and tartrate, with hydroxyl in the vicinity of oxalate and tartrate. The importance of this has been explained in Part I.

In addition to displacing water groups, these anions also displace one another, the order of displacement being that given above, *i.e.*, sulphato will displace chloro groups, and so on. The nature of the acido group and the method of its introduction into the chrome complex affects the properties of the leather produced from a liquor containing such a chromium complex (Gustavson, 1931; Hudson, 1927). The use of a heating treatment in the preparation of a chrome liquor favours the process of olation, and this apparently leads to a lessened affinity of the central chromium atom for the sulphato groups. The removal of acido groups by OH by strong alkali or by over-neutralisation tends to give a leather of rubbery character.

#### SUMMARY.

1. An account of Werner's co-ordination theory of the formation of chromium compounds is given and the present position of the chemistry of chromium is interpreted in terms of the electronic theory of valency, an outline of which is given.

2. Trivalent chromium compounds have a central chromium atom linked by co-ordinate valencies to six other molecules, groups or ions, forming a chromium complex. This complex,

according to the nature of the co-ordinated groups, may be neutral, or positively or negatively charged. The charged complex may be mono-, di-, or tri-valent. The positively charged complexes form salts with the anions of acids; the negatively charged complexes form salts with metallic (and other positively charged) ions.

3. The six co-ordinated molecules or groups may be six water molecules. In this case the complex is positively charged and tri-valent. Negatively charged ions, such as OH, Cl, or  $\frac{1}{2}(\text{SO}_4)$  may penetrate the complex, displacing water molecules and reducing the positive charge. The introduction of three such groups into the complex gives it a neutral reaction. The introduction of four to six such groups gives it a negative charge.

4. Only those chromium compounds which contain OH in the complex can act as tans. Chromium salts hydrolyse in aqueous solution giving basic salts and free acid. These basic salts contain OH in the complex.

5. Increasing the pH value of a chrome solution by adding alkali leads to increased hydrolysis, formation of basic salts and penetration of hydroxyl into the complex. Lowering the pH of a chrome solution by adding acid reverses these changes.

6. The molecules of chromium salts containing water molecules and hydroxyl groups in the complex, tend to become associated through the direct linking of the hydroxyl group already attached to one chromium atom with a second chromium atom. In the formation of this linkage a molecule of water is eliminated. This process is known as *olation*.

Hydroxyl groups in the complex can be titrated directly by acid. Olated hydroxyl groups cannot be titrated directly by acid.

7. The addition of alkali, increase of temperature, or increase in the concentration of chromium favours *olation*.

The addition of acid, a decrease in temperature, or dilution reverses *olation*.

At equilibrium, under certain conditions, 85—90 per cent. of the hydroxyl groups may have passed into the olated form.

8. *Olation* may link up two or more chromium atoms, leading to the formation of complexes of considerable size. Besides *olation*, polymerisation can lead to an increase in particle size.

Particle size is an important factor in deciding whether a chromium salt will tan. Small particles do not have tanning properties; large colloidal particles do not penetrate the collagen fibres. Particles of intermediate size function as tans.

9. Both positively and negatively charged chromium complexes can act as tans. Neutral chromium complexes can also tan.

10. The groups, other than water, which become co-ordinated with the chromium atom in the complex may be arranged in the following series: nitrate, chloride, sulphate, formate, acetate, oxalate and tartrate and hydroxyl.

This series gives the order of ease of penetration into the complex, nitrate penetrating the least readily and oxalate, tartrate and hydroxyl the most readily. Water probably comes between nitrate and chloride.

11. This series also gives the order of resistance of the Ol linkage to the action of acids, nitric acid being least efficient in opening the Ol linkage and oxalic and tartaric acids the most efficient.

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## CHAPTER VII.

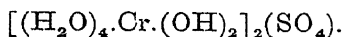
## CHROME TANNING FROM A THEORETICAL ASPECT.

## INTRODUCTION. \*

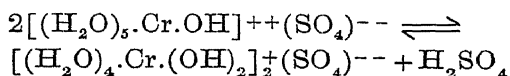
IN dealing with the chrome tanning process from a theoretical standpoint, it is proposed, before passing on to describe the various theories of chrome tanning, to consider briefly the composition of and the active groups in the reacting materials and the changes which can occur in these during the tanning process.

*(a) Composition of and active groups in the chrome tanning salt.*

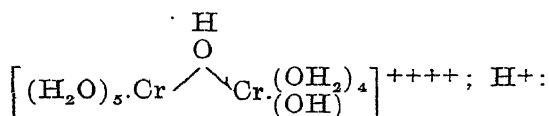
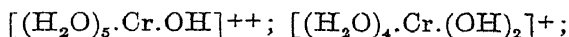
The reacting materials can be divided into tanning material (chrome tanning liquor) and material being tanned (hide substance or collagen). In a very simple case, the tanning material will consist of the tanning salt of an average composition, represented by the formula  $[(\text{H}_2\text{O})_5.\text{Cr}.\text{OH}]\text{SO}_4$  dissolved in water. This salt has a basicity of 33 per cent., that is 33 per cent. of the  $\text{SO}_4$  present in chromium sulphate  $[\text{Cr}(\text{OH})_6]_2(\text{SO}_4)_3$  has been replaced by OH. The presence of such an OH group appears to be the first essential in a chrome tanning salt, which must also be soluble in water, or the chromium compound, if it contains no OH group, must, when dissolved in water, produce a salt containing an OH group. This OH group is not ionised but reacts with acids instantaneously, that is, it can be titrated. It resembles, therefore, the OH groups in any weak base. The presence of  $\text{H}_2\text{O}$  in the chrome complex also appears to be essential. It has been pointed out that in chrome complexes where OH and  $\text{H}_2\text{O}$  are present in the same molecule, one hydrogen atom from the co-ordinated water molecule can ionise. The chrome complex, therefore, has both acid and basic properties. The solution of 33 per cent. basic chromium sulphate mentioned above will contain, in addition to free sulphuric acid resulting from hydrolysis, the chromium salt



Chromium salts (aquo salts) in solution undergo a change in the structure of the chromium complex owing to the great ease with which OH replaces  $H_2O$  molecules. This change may be represented as follows:—



According to Bjerrum, a portion of the basic chromium salts becomes latent or, according to Stiasny, the salts "olate" and form "Ol" compounds containing OH groups which do not react readily with acids. The extent of the occurrence is discussed later. The chrome tanning solution will, therefore, contain the following types of kations:—



and  $(SO_4)^{--}$  anions.

The composition of the complex chromium kations can be altered by the heating treatment which the solution of basic chromium sulphate has received in its preparation, and by the concentration of the solution, to mention but two factors, so that they may contain  $SO_4$  groups in the complex. The pH value of a chrome liquor is also affected by the manner in which the liquor is treated (Blockey, 1918). According to Stiasny (1928), a solution of normal chromium sulphate (10 g. chromium per litre and 0 per cent. basic) which has an initial pH value of 2.81, on boiling for 5 minutes then has a pH value of 1.21. If the freshly prepared solution is allowed to stand for 4 weeks, the pH value has fallen to 2.12, and the solution gives a difference figure of 0.67 on tenfold dilution, whereas the fresh solution or the solution after 72 hours gives difference figures on tenfold dilution of about 0.36. An account has already been given of the way in which this liberation of hydrogen ions (increase in acidity) may take place, and since the changes involved are brought about by the breaking up and rearrangement of co-ordinate links they would not take place instantaneously, but gradually, and the liberation of acid will, therefore, be continued over a period of time. A similar set of figures is available for a 33 per cent. basic chromium sulphate solution (10 g. chromium per litre) which has a pH value of 4.24 when freshly prepared, falling to 2.97 in 4 days and 2.93 in 4 weeks. This solution, on boiling, has a pH value of 2.35, which, after 5 months' standing at laboratory temperature, rose to 2.93. The pH value of about 2.95 can, therefore, be considered as the equilibrium pH of this solution on standing. An important feature of the freshly boiled solution is that on tenfold dilution the pH value rises only 0.48 units, which goes to show either that the 33 per cent. basic solution of chromium sulphate does not contain any large amount of a strongly ionised acid, namely, sulphuric acid, or that the solution is well buffered by the chrome salts which are present. That the extent to which olation occurs is

of considerable magnitude will be realised from some recent work by Stiasny and Königfeld (1932) which has shown that in a 33 per cent. basic chromium sulphate solution (10 g. chromium per litre), 89 per cent. of the basic groups are latent or olated after the solution has stood at room temperature for 5 days. At one-tenth of this concentration, the percentage of olated basic groups is 83 per cent. and at threefold concentration, is 94 per cent. An increase in temperature to 75°C. for 5 hours raises the percentage of olated basic groups to 100 per cent. The addition of sodium chloride to the 33 per cent. basic chromium sulphate has no effect on the amount of olation, whereas the addition of sodium sulphate increases somewhat the percentage of olated basic groups. Both or either of these salts are present in commercial chrome tanning liquors, the former added in the early stages and brought in by pickled goods and the latter as a by-product in the manufacture of the chrome liquor.

A further point which arises from a consideration of these results is the apparent small proportion of unolated basic chromium salts in a 33 per cent. basic chromium sulphate solution which are in a state to suffer hydrolysis in water, namely about 15 per cent. of the total hydroxyl groups. The remainder, the olated portion, is only acted upon slowly by acids in the cold and presumably could be considered to diffuse practically unchanged into the material being tanned. Because of their stability towards acids, it is possible that the Ol compounds would undergo an increase in particle size within the pelt, become more colloidal and thereupon act as tanning agents. It would seem likely that a considerable amount of the chrome salt in chrome leather is present as a basic chrome salt in which the hydroxyl groups are olated.

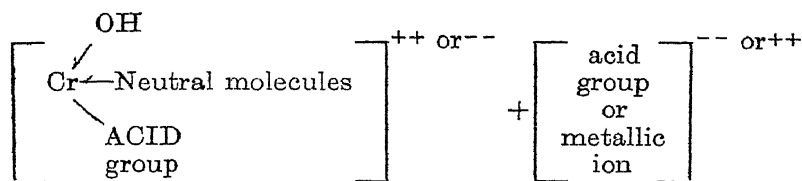
It is also of note in connection with the question of the possibility of free acid being present in a 33 per cent. basic chromium sulphate solution that the equilibrium pH of this solution, about 2.93, is greater than the pH value, 2.81 of a freshly prepared normal chromium sulphate solution of the same chromium content.

If the assumption be made that the whole of the hydrogen ions in the 33 per cent. basic chromium sulphate liquor at a pH value of about 3.0 arise through hydrolysis, then the concentration of sulphuric acid is about  $N/1000$  or 0.049 g. per litre. The solution also contains 10 g. of chromium per litre. That is, for 52 g. of chromium there are 0.25 g. of free sulphuric acid or per 1 g. atom of chromium there are about 0.0026 g. molecules of sulphuric acid. The maximum amount of free sulphuric acid in a 33 per cent. basic chromium sulphate solution is, therefore, very small compared with the chromium concentration. It is probable that this is also the case in ordinary 33 per cent. basic chrome tanning liquors in general. This point also receives support from the fact that such liquors do not exert any considerable plumping action on pelt placed in them. The amount of acid is greater in liquors which are less basic and these bring about plumping because of their lower pH value. This is one of the reasons for starting the tannage in liquors of lower basicity than 33 per cent. where a certain amount of plumping of the pelt is found desirable in the early stages of tanning.

## THE CHROME TANNING PROCESS

The hydrolysis of a chromium salt, as would be expected, proceeds very rapidly when the free acid is neutralised by alkali and presumably this is also the case when the acid is fixed by the hide substance. This continuous removal of hydrogen ions from the 33 per cent. chrome tanning liquor and their rapid continuous replacement in the liquor by hydrolysis of the chrome tanning salt are obviously of the greatest importance in the mechanism of chrome tanning.

From the above brief outline it will be realised that the composition even of the simplest chrome tanning solution is very complicated. The picture becomes much more intricate in dealing with commercial chrome liquors. These, in addition to the salts enumerated above, can also contain added alkali salts, groups such as  $\text{SO}_4$  within the chromium complex, masking substances such as oxalates, etc., hydroxy acids and volatile and non-volatile acids produced in the reduction of dichromates. Part of the chromium complexes may be in the electronegative state, particularly in commercial tanning extracts. This may be represented pictorially as follows:—



that is, the complex chromium ions may be electropositive or electro-negative or both states may be present and it may be linked electro-valently with acidic groups or metallic ions. The grouping within the complex can contain the hydroxyl group (this appears to be essential), neutral molecules, such as water molecules, acidic groups, such as  $\text{SO}_4$ , and so on, all of which are co-ordinately linked to the chromium atom and the displacement of which from the chromium complex generally affects its nett electrical charge. Furthermore, the greater proportion, over 80 per cent., of the hydroxyl groups are latent or olated.

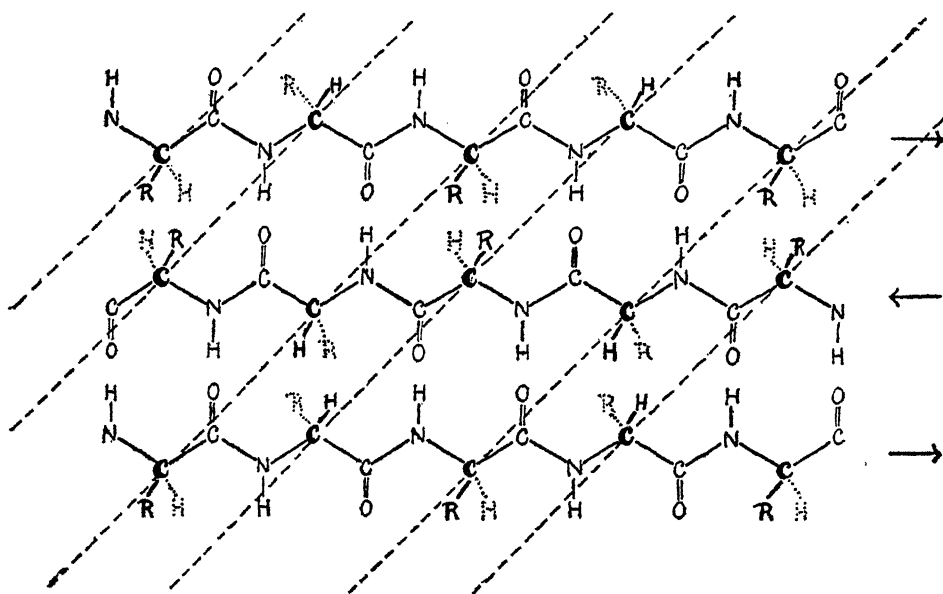
Whether the chrome tanning liquors can be regarded as being colloidal *after* their diffusion into the hide substance is a question which is difficult to answer. F. L. Seymour Jones (1922) subjected a basic chromium sulphate liquor, prepared from dichromate and sulphur dioxide and then boiled, to ultra-filtration and showed that the liquor was not colloidal. Basic chromium nitrate solutions can contain very complicated chromium complexes of high molecular weight (see Table V). According to Stiasny and co-workers (1923 onwards) the chrome tanning complex must be semi-colloidal; moreover, tanning power increases with the molecular size of the chromium complex which is a function of the basicity of the liquor and the degree of olation. Chrome tanning liquors are thus to be regarded as semi-colloidal and after diffusion within the hide substance they may, on account of the basic properties of the collagen which would favour olation, approach more nearly to the colloidal state which would prevent their re-diffusion out of the hide substance and into the tanning liquor.

*(b) Composition of and active groups in the collagen.*

The second party in the chrome tanning process, the material being tanned (collagen), is a hydrated colloidal structured protein. It contains the elements carbon, hydrogen, oxygen and nitrogen. The oxygen atoms of protein molecules are present as carboxyl, amide and hydroxyl groups, the nitrogen atoms as amide, imino and amino groups. "In all these groups (Jordan Lloyd and Phillips, 1933) both oxygen and nitrogen atoms possess electrons which are not utilised in covalent linkages and may, therefore, co-ordinate with water molecules. In addition, the hydrogen atoms of these groups may form co-ordinate links with the unshared electrons of the water molecules. The hydration of proteins in water is due to the co-ordination of water molecules with the oxygen, nitrogen and hydrogen atoms of the hydroxyl, carboxyl, amino, amido and to a lesser extent, the imino and keto groups." The active groups present in hide substance can, therefore, be divided into basic groups, such as  $\text{NH}_2$ ,  $\text{NH}$ ; acidic groups such as  $\text{COOH}$ ,  $\text{OH}$  and according to Page (1933), the peptide groups in their tautomeric form,  $-\text{C}=\text{N}-$ .



All these groups will be dehydrated (see below).

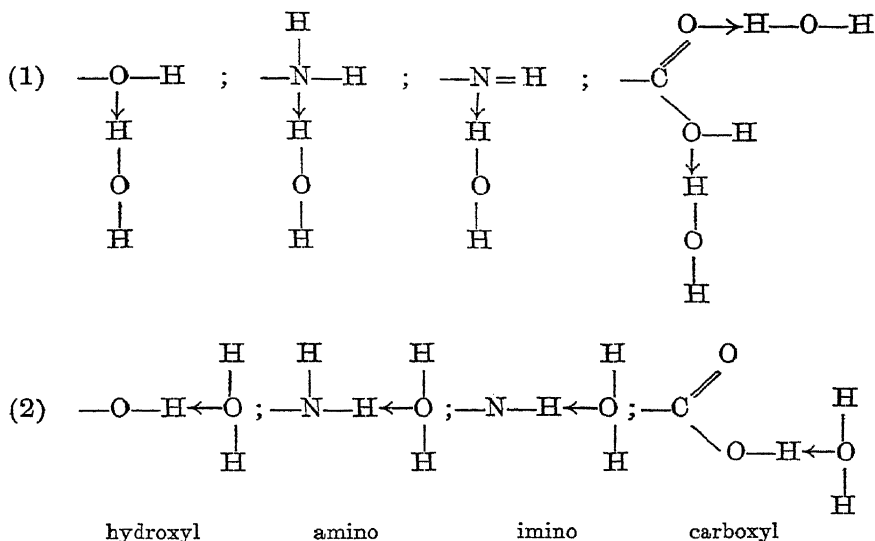


The solid "H" and "R" groups on the asymmetric carbon atoms lie above the plane of the paper. The dotted "H" and "R" groups lie below the plane of the paper.

FIG. 5.

According to the most recent ideas (Jordan Lloyd, 1934), collagen is built up of very long molecules lying side by side. Fig. V shows three long molecules lying side by side. Each

molecule can be regarded as having a long zig-zag backbone and a number of projecting limbs or side-chains, marked R in the diagram. Some of these R groups are chemically inert and some are chemically active. Some of the chemically active R groups have definite acid properties; others have basic properties, *i.e.*, they behave like alkalis. The following illustrations show some of the ways in which water molecules may hang on to the protein.



Further, some of these projecting limbs have the property of linking up with others on adjacent molecules; for instance, the acid and basic groups can come together to form cross linkages of the salt type. If now these very long molecules be arranged side by side, a considerable amount of cross linkage occurs between the projections or limbs or side groups, as we prefer to call them, of adjacent molecules. The groups project sideways from the backbone and limit the closeness with which the latter can be packed together. The resulting structure constitutes a fibril. The fibril so formed, with its parallel arrangement of backbones and cross linkages between side groups, therefore, has a more or less open structure like a three-dimensional grid, and water and other molecules can wander into and through the meshes. Small molecules will wander through this netlike structure more easily than large ones.

There is another important property common to all proteins and which is characteristic of the backbone. The backbone is formed of a series of segments joined by peptide links,  $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{N}- \\ | \\ \text{O} \end{array}$  and

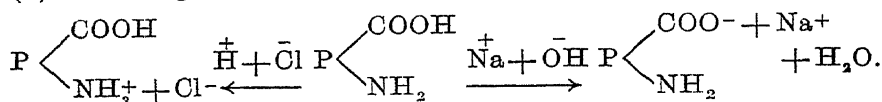
this type of link is readily attacked by the digestive enzymes pepsin and trypsin, and the enzymes secreted by bacteria. Under the action of these enzymes the long firm molecules or backbones are broken up at the peptide links into short disconnected pieces. When this happens to collagen molecules, the long parallel back-

bones comprising the fibrils break up into smaller pieces, the fibril in turn breaks up, and the fibres, which are composed of bundles of parallel fibrils, go to pieces and ultimately liquefy.

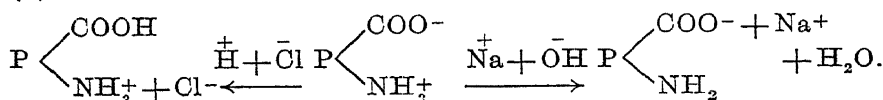
Of recent years, the conception of proteins, known as the Zwitterion concept (see Jordan Lloyd, 1933) has received increasing attention. Experimental evidence points to the fact that if there are present in a solution amphoteric substances such as amino acids, polypeptides or proteins in the electrically neutral or iso-electric condition, then their properties are better represented by the Zwitterion formula,  $\text{NH}_3^+\text{P.COO}^-$ , with the opposite charges apparently balanced, than by the classic formula  $\text{NH}_2\text{P.COOH}$ . Such ions which are at the same time positively and negatively charged are called zwitterions. They have at the same time both acid and basic properties. At low pH values, hardly any uncharged  $\text{NH}_2$  groups exist in collagen, and even at the iso-electric point the amino groups are present to about 65—70 per cent. as  $\text{NH}_3^+$  ions (charged centres) and only 30—35 per cent. as uncharged amino groups (Page, 1933).

The action of acids and alkalis upon a protein can be represented as follows:—

(1) according to the classical equation,

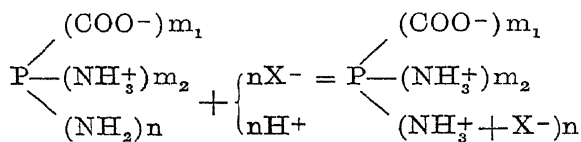


(2) in the zwitterion form,

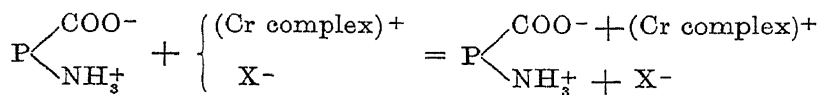


The addition of acid affects the carboxyl groups, tending to transform the charged  $\text{COO}^-$  groups into uncharged  $\text{CO.OH}$  groups. Conversely, the addition of alkali tends to transform the charged  $\text{NH}_3^+$  groups into uncharged  $\text{NH}_2$  groups.

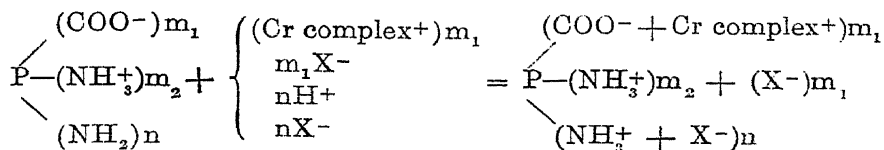
In the case of a protein with both charged and uncharged amino groups, acid is taken up as follows:—



By analogy, the reaction between a positively charged complex chromium ion and a simple amino acid may be pictured,



Thus the reaction, as far as the amino and carboxyl groups are concerned, between collagen and chrome liquor may be represented by,



The hydrogen ions shown in this equation arise from the hydrolysis of the chrome salt. They may, of course, arise from the previous pickling of the collagen with acid and salt, which would lessen the fixation of hydrogen ions in the chrome bath, resulting in a lessened fixation of chromium. A similar lessening in the chromium fixation would result if the amount of  $\text{NH}_2$  groups in the protein is reduced by deamination and so on.

As chrome tanning occurs on the acid side of the iso-electric point of collagen, the amount of ionised  $\text{COOH}$  groups would be exceedingly small, whilst that of charged amino groups would be great. It is, therefore, extremely improbable that chrome tanning, *i.e.*, chrome fixation, will involve an electrovalent link between the chrome complex and the carboxyl groups. For the  $\text{COOH}$  groups to be involved, the resulting chrome compound would have to have a very pronounced insolubility (chrome leather has this property). The possibility has, however, been considered, notably by Gustavson, whose opinions are summarised below.

That peptide linkages are involved in chrome tanning, is stated by Thomas and F. L. Seymour Jones (1924), who observed that a kationic chrome tannage imparts to hide powder a complete resistance towards tryptic digestion, whereas hide powder tanned with vegetable tannins, quinone, formaldehyde and copper sulphate were digested (see also Bergmann, Pojarlieff and Thiele, 1933). The action of trypsin is generally considered to be a hydrolytic scission of peptide linkages, although, according to Merrill (1933) it is not certainly known that the breaking of the peptide linkage ( $-\text{NH}-\text{CO}-$ ) is the sole chemical change produced by trypsin. Where the tanning agent combines only with the carboxyl groups, as with copper, tryptic digestion is as great as with untanned collagen; where the tanning agent, such as formaldehyde and quinone, combines with the amino groups of the collagen, the amount of digestion depends upon (1) the type of tannage and (2) the amount of the tanning agent combined with the collagen. From these results, the possibility of combinations of the tanning agent at the peptide link has to be borne in mind.

### (c) *The Course of the Chrome Tanning Process.*

The one-bath chrome tanning process, shorn of its practical details, consists in the bringing together of the chrome tanning liquor and the collagen; that is, bringing a semi-colloidal solution (the tanning liquor) into contact with a protein structure having the properties of a semi-permeable membrane. The first action which occurs is the diffusion into the collagen of the smallest ions and the more acid constituents of the tanning liquor. According

to Thomas, Baldwin and Kelly (1920), at first the absorption of acid is about twice that of the chromium, but after the initial period of 1 hour, the speeds of both reactions are practically the same. This has been experimentally confirmed (Second Annual Report of the British Leather Manufacturers' Research Association). Using a chrome tanning liquor of a basicity of 33 per cent., the average basicity of the chromium compound which had been taken up by the hide substance was 7 per cent. at the end of 1 hour, that is, more acid than the original chrome liquor. From then on, the basicity within the hide substance rose slowly and after about 6 hours reached 33 per cent. During these changes, the basicity of the tanning liquor rose, and after 1 hour was at about 50 per cent. It then fell slowly to about its original value of 33 per cent. About one-half of the tannage had been achieved at the end of the first hour. From these considerations and remembering that a 33 per cent. basic chromium sulphate liquor contains very little free sulphuric acid relative to the chromium content (calculated from the pH value of the liquor) it would appear proven that the low basicity of the chromium salt in the material being tanned is the result of a differential diffusion into the hide substance of the more acid constituents of the tanning bath (see also Stiasny, 1908). The small amount of sulphuric acid in the tanning bath diffuses more rapidly into the pelt than the chromium salt. The sulphuric acid is fixed by the hide substance, that is, it is removed from the tan liquor still outside the hide substance. This liquor undergoes continuous hydrolysis, producing further amounts of acid which in turn continuously diffuse into the pelt. The result of this chain of reactions is as found in the practical investigation, namely, that the basicity of the chrome salt within the hide substance, by virtue of the take-up of sulphuric acid, is lowered and that of the remaining chrome tanning salt is raised. If the continuous withdrawal of acid from the tanning liquor is excessive, it can bring about such a raising of the basicity of the chrome tanning salt that it precipitates out in the tanning solution. As might be expected, the presence of initial amounts of acid in the hide substance derived from the previous pickling process has a retarding influence on the subsequent uptake of chromium.

The fixing of the acid by the collagen is most probably related to the basic groups in the protein. According to a recent publication by Phillips (1933), the interaction of proteins with acids and bases is more complex than the interaction of a simple base with an acid or of a simple acid with a base. Jordan Lloyd and Mayes (1922) and Atkin and Douglas (1924) found that gelatin will fix a greater amount of either acid or base than would be expected on the assumption that proteins combine with acids and alkalies only through their free amino and carboxyl groups respectively. Such observations have been explained by assuming that the peptide linkage of the protein (CONH) is involved in the interaction. This excess fixation does not, however, occur until the pH value is less than 2, which is generally beyond the acidity used in tanning. According to Hitchcock (1925), 1 g. of the protein gelatin, which is closely related to collagen, will take up approximately  $89 \times 10^{-5}$  molecules of acid. Deamination reduces this acid fixing capacity

to about one-half ( $44 \times 10^{-5}$  molecules). The figures for hide powder are similar. In the Third Annual Report of the British Leather Manufacturers' Research Association it was shown that approximately 3.8 per cent. of the total nitrogen is present as primary amino groups (the corresponding figure for gelatin is 3.1 per cent.).

The increased basicity of the chrome tanning salt due to the withdrawal of acid also increases the average molecular size of the chromium salts in the solution in that it increases the extent to which olation occurs (an increase in the basicity of a chromium salt brings about increased olation).

These changes in the molecular aggregation of the chrome tanning salt are the fundamental points underlying the deposition theories of chrome tanning, involving the formation of a protective deposit of a chromium salt in and about the fibres of the material being tanned and theories based on the molecular size of the chrome tanning salt.

Furthermore, if the basic groups of the hide substance are modified, that is, their capacity for taking up acid is affected by the pre-treatments to which the hide substance has been subjected before tanning, such as liming, bating, vegetable tanning, deamination and so on, this should have an effect on that part of the tanning process which is inter-related to the basic groups of the hide substance. This point is considered further in Appendix A, which deals with the effect of various pre-treatments of the collagen upon subsequent chrome tanning and the bearing of these upon chrome tanning theories.

In the case of chromium liquors containing complex chromium anions, it is possible to conceive of an interaction between the basic groups of the collagen and the acidic chromium anion, which will be related to the amount of and rate of formation of these acidic chromium complexes. These ideas and their opposite, namely that the acidic groups of the collagen interact with the basic or electropositive chromium complexes, have formed the basis of what might be termed the salt formation theories of chrome tanning.

#### (i) DEPOSITION THEORIES OF CHROME TANNING.

In the Introduction to this Chapter attention has been drawn to the following features in the chrome tanning process, the diffusion of acid and chrome tanning salt into the hide substance, the fixation of the acid by the hide substance and the effect of this on the chrome tanning liquor, both within and outside the hide substance. Many theories of chrome tanning have been built around these changes. Particular mention may be made of the suggestion that the withdrawal of acid from the tanning liquor which has diffused into the hide by the hide substance brings about a precipitation of an insoluble chromium salt.

Knapp, in 1858, was the first to attempt an explanation of chrome tanning on this basis. According to his theory, chrome tanning consists in a deposition of chromium hydroxide or strongly basic chromium salts on the surface of the fibres. The fibres are thus coated with water-resisting materials, which prevent swelling

and putrefaction. The fact that increasing basicities in the chromium liquors make the precipitation of insoluble chromium compounds easier, and at the same time increase the amount of chromium deposited on the fibres, was entirely in harmony with this theory. A further support to this theory was forthcoming when it was found that chrome leather could be dechromed, that is, chrome tanning could be reversed. Procter (1910) supported the view "that the free acid in a chrome liquor is fixed by the hide fibre and that the hydrolysis of the chrome salt is carried to the point where the basic salt becomes colloidal and insoluble in water and forms a coating or possibly an adsorptive or chemical compound with the fibre, which is thus prevented from swelling or adhesion." According to his views, "in a one-bath basic chrome tanning process, the hydrolysis of the normal chrome salt is such that the fixation of small quantities of acid by the hide causes the fixation of comparatively large quantities of basic chrome salt." Whether the chromium exists in the hide as oxide, hydroxide or very basic salt and what is the nature of the tanning effect, was, according to Procter, not yet definitely determined. It was realised, however, that an alkaline condition at once renders chrome leather horny and apparently under-tanned. The observation of Chabrié (1892) that colloidal solutions flowing through a capillary deposit part of their colloidal dissolved material on the walls and, as it were, tan these, was again in harmony with the deposit ideas. A. Seymour Jones (1915) examined chrome leather under the microscope and found that the fibres were "plated" with an oxide of chromium, leaving the interior structure still untouched, and that in badly chromed leather the plating was less heavy and absent on the internal and smaller fibres. This observation has, however, not been confirmed. A further point claimed in favour of the Knapp theory which, however, loses weight in that it is also claimed to support other theories of chrome tanning, is the absence of stöchiometric proportions between hide and tanning material. The real point of the Knapp theory, namely, that chrome tanning is merely a surface phenomenon depending upon isolating the fibres and keeping them isolated without any penetration of the tan into the fibre or interaction with the fibre material has not, however, maintained itself as correct. Further light on this problem was available when it was found possible to examine the fine structure of fibres more accurately. This progress was made possible by the use of the microscope fitted with a polariscope. Küntzel (1926), using this method, claimed to have found that the tan was able to penetrate within the fibrils, to change the micelles and thereby alter their optical constants. This would appear to support the view that in chrome tanning one is not dealing with the simple surface deposition of the tan on the outside of the fibres or fibrils but with a chemical interaction. Körner (1905) has suggested, however, that tanning leads to the formation of a solid solution of the tan in the collagen and attributes the resistance of the leather to water to the low diffusion properties of the tan. Theories which are based on the assumption of a primary surface action (adsorption) with secondary processes of various kinds, whereby the gradual penetration of the tan into the fibre is brought about, can also readily be brought into line with Küntzel's observation.

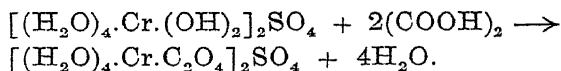
It is of interest under this type of theory to recall that the theory advanced in 1922 by the British Leather Manufacturers' Research Association as a working hypothesis (Second Annual Report, p. 73 *et seq.*; Seventh Annual Report, p. 50) was based on the assumption that chrome tanning consists of a deposition of the basic chromium sulphate  $[(\text{H}_2\text{O})_4\cdot\text{Cr}(\text{OH})_2]_2\text{SO}_4$ , in and around the fibres. Part of this basic salt combines chemically with the collagen, possibly by an interaction involving the  $\text{NH}_2$  groups of the collagen and the OH groups in the basic chrome salt. The following points were advanced in support of this theory:—

- (1) The basicity of the chromium salt (calculated from the amounts of chromium and  $\text{SO}_4$ ) in finished one-bath chrome leather is very close to that of the above basic sulphate, *i.e.*, 66.7 per cent.
- (2) The particular basic sulphate postulated can be prepared by the addition of a weak base, pyridine, to a solution of chrome alum and sodium sulphate.
- (3) Collagen, it was suggested, could act as a weak base and precipitate this basic sulphate from a chrome tanning liquor (in and around the fibres) in a similar manner to the precipitation of this salt from chrome alum by pyridine.
- (4) In making chromium sulphate basic with sodium hydroxide, a temporary precipitation of the difficultly soluble  $[(\text{H}_2\text{O})_4\cdot\text{Cr}(\text{OH})_2]_2\text{SO}_4$  occurs at 14 per cent. basicity. (With chromium chloride, a temporary precipitation of chromium hydroxide occurs at 30 per cent. basicity.)

Chrome leather in the blue was thus regarded, according to the Research Association's theory, as consisting of deposited basic salt and a compound of this with collagen.

The following further points lend considerable support to the theory.

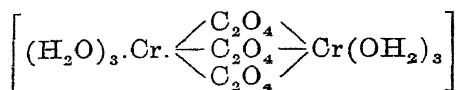
The basic chromium sulphate  $[(\text{H}_2\text{O})_4\cdot\text{Cr}(\text{OH})_2]_2\text{SO}_4$  is almost insoluble in water; when fresh it is very soluble in oxalic acid and on ageing, either when kept warm, moist or dry, becomes less and less soluble in oxalic acid. The action of oxalic acid upon this basic chromium sulphate is, according to Stiasny (*Gerbereichemie*, p. 393) as follows:—



If chrome leather in the blue be treated with oxalic acid, then under particular conditions about one-third of the total chromium is not easily removed unless the temperature of the treatment be raised. It was suggested that the portion easily removed was the deposited, unchanged basic salt, which is very easily dissolved by oxalic acid when freshly deposited, and that which is combined with the collagen is not so easily removed.

A difficulty in drawing conclusions from experiments in which chrome leathers were dechromed by oxalic acid is the fact that hexa-aquo-chromi oxalate is insoluble in cold water but dissolves

readily in hot water, forming a green compound the constitutional formula of which is probably



Thus, the finding that a portion of the chromium is not easily removed by the action of oxalic acid until the temperature is raised may be attributed to the conversion of part of the chrome tanning salt into insoluble chromium oxalate.

The proportion of chromium not easily removed from chrome leather by treatment with oxalic acid increased if the chrome leather was dried and heated. A slight increase was found at 21°C. and a considerable one at 105°C. The basic chromium salt  $[(\text{H}_2\text{O})_4 \cdot \text{Cr}(\text{OH})_2]_2\text{SO}_4$  exhibits similar properties when similarly treated.

The most striking feature of the experiments on this more firmly held chromium was the fact that the proportion of firmly held to total chromium remained practically constant, about 33 per cent., throughout a laboratory tanning process in which a one-bath kationic chrome liquor was used.

It was also found that the effect of deamination of the pelt before chrome tanning was to reduce not only the total chromium taken up under specified experimental conditions but also, in a proportional amount, the quantity of difficultly removable chromium. The decrease in the latter figure was not sufficiently emphatic to show whether this chromium is combined with the hide substance or whether it is present in an "aged" modification of the basic chromium sulphate  $[(\text{H}_2\text{O})_4 \cdot \text{Cr}(\text{OH})_2]_2\text{SO}_4$  which is deposited and not combined.

Subjecting the pelt to a pre-tannage with formaldehyde or sumac (and then chrome tanning) was also found to reduce the total amount of chromium taken up but did not greatly affect the proportion of difficultly removable chromium to total chromium.

It was, however, finally not found possible to differentiate between deposition, combination of chromium with the collagen and ageing, in accounting for the differential behaviour of the chromium in one-bath chrome leather towards oxalic acid.

It does seem certain, however, that the chromium in one-bath chrome leather is in two distinct forms, one of which, about double in amount to the other, reacts readily with oxalic acid to give a soluble salt, while the other reacts only slowly with oxalic acid at the ordinary temperature but more readily if the temperature be raised.

An important point which arises in respect of the deposition of the 66.7 per cent. basic chromium sulphate in the material being tanned is that the preparation of this salt from a 33 per cent. basic chromium sulphate has not yet been achieved. Furthermore, if in the preparation of the 66.7 per cent. basic salt from chromium sulphate, using pyridine as precipitating agent, the chromium sulphate solution is not used when freshly prepared but allowed to stand overnight, the chromium salt which is precipitated by the addition of pyridine is only about one-fifth of

the quantity obtained if the freshly prepared chromium sulphate solution be used and its basicity is much greater than 66.7 per cent. Allowing the chromium sulphate solution to stand has undoubtedly allowed hydrolysis and olation to occur with the additional probability that  $\text{SO}_4$  groups have wandered inside the chromium complex, partly as a result of the addition of sodium sulphate.

This differential behaviour of chrome leather towards oxalic acid may be explained by the assumption that that part of the chrome tan which is insoluble in oxalic acid is held to the collagen by an OH bridge similar to that which is formed between two chromium atoms by olation. The olation change is assisted by the withdrawal of acid from the basic chrome liquor by the collagen, and is furthermore accompanied by the displacement of co-ordinated water molecules from both reacting substances, that is to say, both basic chrome salt and collagen. The loss of water from the collagen, it is suggested, might account for the resistance of chrome leather to the action of boiling water.

Thus chrome leather could contain, on this suggestion, deposited basic chromium salts with hydroxyl (OH) groups which react readily with a cold solution of oxalic acid. These basic salts may be linked to the collagen so that they do not react with oxalic acid except when the temperature is raised. There are also the possibilities that the combination between basic chromium salt and collagen might be with the  $\text{COOH}$  of the collagen, forming a salt which with cold oxalic acid would give chromium oxalate (insoluble in cold water and, therefore, not removed from the leather) or consist of a co-ordinately combined linkage which would be broken by the oxalic acid (which readily enters the complex), giving collagen and a soluble chromium salt with oxalic acid inside the complex.

The relative amounts of deposited chromium and combined chromium will depend upon the capacity of the collagen to produce the basic salt by withdrawing acid from the tan liquor. The amount of combined chromium will depend upon the extent to which the basic salt can combine by co-ordination with the collagen. The theory does not exclude the possibility that the co-ordinate valencies of the collagen may be exerted through nitrogen atoms and that the electro-valences, with electronegative chromium complexes, may be exerted through the basic groups of the collagen.

According to Elöd and Siegmund (1928), the hydrolytic acid in a chrome tanning liquor enters into salt formation with the basic groups of the pelt. This brings about an alteration in the particle size in the liquor which has diffused into the pelt with the formation of particles, basic salts, within the leather structure of such a size that they do not diffuse out. That is, tanning is achieved by the formation of particles of a suitable degree of dispersion, consisting of structures which are more or less stable, provided these particles are suitably and homogeneously dispersed in the leather. Besides chromium hydroxide, suitably basic compounds (complex or otherwise) can tan if they attain to particles of a suitable size within the leather fibre. If the acid-combining capacity of the hide is lessened in any way by linking up the

amino groups with acid (pickling), vegetable tannins, quinone or formaldehyde or by removal of the amino groups (deamination), then the continued hydrolysis of the chrome salt is lessened and the chromium uptake reduced.

In a later publication, Elöd and Cantor (1934) state that it is essential that each individual collagen fibril, even in the middle layer of the pelt, should react with the tanning material. This involves the diffusion of the chrome tanning agent in the crystalloidal state, followed by changes which bring about tanning. In order to maintain the crystalloidal condition of the liquor it is customary to use regulators (masking substances, pickling, etc.). During the tanning process the crystalloids (molecular dispersion) which are present in the hydrolytic equilibrium are altered by (a) the combining of the protein with acid and (b) membrane action (membranwirkung) whilst the semi-colloidal and colloidal particles are deposited (abfiltriert) on the surface of the constituents of the fibres. These changes are assisted by washing, neutralising, etc., and lead to the formation of the real tanning substances. These contain hydroxyl and they can even consist of pure hydroxides (cobalt hydroxide, chromium hydroxide, etc.), but this is not essential. Their tanning action consists in that they enter into co-ordinate linkage with the active points of the protein molecule. In addition, further amounts, for example of chromium compounds, can be deposited in the collagen. Whether these additional amounts are of vital importance for the actual tanning which is usually assumed to require only small amounts of chromium, or whether it affects such properties of the leather as feel, boiling test resistance etc., and also whether these additional amounts (because of their particle size) are merely deposited or whether they form co-ordinate linkages, has still to be explained.

Burton, in 1922, suggested that chrome tanning involves three reactions:—

- (1) The absorption of the liquor by the pelt, *i.e.*, the filling of the spaces between the fibres with liquor.
- (2) The adsorption or rather chemical combination of the free acid with the pelt, thereby endowing the latter with a positive charge,  $\text{PNH}_2 + \text{HCl} = \text{PNH}_3^+ + \text{Cl}^-$ .
- (3) The removal of free acid, leading to further hydrolysis so that the basic salt will become insoluble in water and be deposited on the fibres, but whether this was a case of adsorption or whether a chemical compound was formed between the chromium and the COOH groups of the collagen was an open question.

Burton postulated that if a chrome liquor can be regarded as a colloidal solution of basic chromium salts or chromium hydroxide and if the chromium compound is negatively charged (due to the absorption of  $\text{SO}_4$  ions which are in excess in the liquor between the fibres), chrome tanning may consist of a co-precipitation with the positively charged pelt.  $\text{PNH}_3^+ + (\text{Cr compound})^- = \text{tanned leather}$ . The affinity of the hide for chromium and, therefore, the amount taken up would increase with the acid absorption up to a certain limit, *i.e.*, until the hide fibre or collagen has absorbed

its complete equivalent of acid and become completely converted to the positively charged colloidal ion. After that, the excess acid simply competes for the chromium and this retards and reduces the absorption of chromium. The nature of the negatively charged chromium compound and the conditions favourable to its formation are obviously of vital importance since speed of tanning will be determined by the speed of the co-precipitation of this with the positively charged pelt. The amount of negatively charged chromium compound will be decreased by adding acid and increased by adding alkali. The changing of the well-known blue colour of a chromed skin to green on neutralising or drying is to be attributed to some later chemical changes.

Following the work of F. L. Seymour Jones (1922) on the ultra-filtration of a basic chromium sulphate solution (made from dichromate and  $\text{SO}_2$  and boiled), which showed that the solution was not colloidal and in view of the fact that neutralised solutions of green chrome alum and all basic chromium chloride solutions do not contain negatively charged chromium complexes, Burton (1924) rejected the conception of one-bath chrome tanning as a purely colloidal process, involving the mutual equalising of the electrical charges of the collagen and the tanning material. According to Procter and Wilson (1916), the mutual precipitation of oppositely charged colloids appeared tenable to some extent for vegetable tanning as the collagen at the usual pH values of vegetable tan liquors (that is, below pH 5) is charged positively whilst the vegetable tans, as weak acids, have a negatively charged colloidal ion. The theory (Stiasny, 1931) cannot be directly and completely applied as it stands to ordinary chrome tanning since the most commonly used chrome liquors contain kationic chromium complexes, *i.e.*, are positively charged and an equalising out of electrical charges is not possible.

#### (ii) SALT FORMATION THEORIES OF CHROME TANNING.

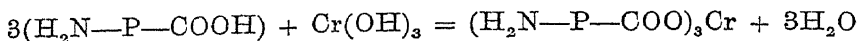
Suggestions that there is chemical interaction between hide proteins and chrome salts have played a considerable part in many of the theories of chrome tanning.

One of the most prominent is the "salt" formation theory. In this, the hide, through its acidic groups or basic groups reacts with the kationic chromium complexes or anionic chromium complexes in the chrome tanning liquor respectively. For the reactions of collagen as a base, the primary amino groups are available, whilst for the reactions as an acid there are the carboxyl groups. Fahrion (1903), introduced an unnecessary complication to the "salt" formation theory in the assumption that the hide must first undergo oxidation before it interacts with the tan forming the leather salt, and this part of his hypothesis is rejected by Stiasny (1908).

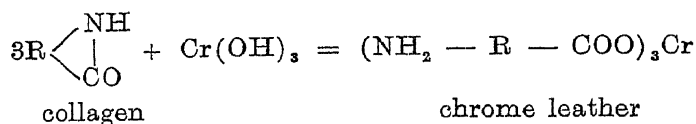
##### (a) *Salt formation at the Acid Groups of the Collagen.*

The simple salt formation theories of Thomas and Kelly (1921-1924) and Wilson (1929) assume that the free carboxyl groups of the collagen react as an acid with chromium hydroxide or with basic kationic chromium complexes acting as bases, giving rise to chromium collagenates. As chrome tanning takes place on the

acid side of the iso-electric point of collagen, the amount of ionised COOH groups would be exceedingly small, whilst that of the  $\text{NH}_2$  groups would be great, so that the equation representing the change, namely



can only satisfactorily represent the reaction between collagen and chromium hydroxide if the solubility of the chromium salt produced is considerably less than that of other possible chromium compounds (basic chromium salts). Wilson's descriptive equation goes still further, as follows:—



for he regards collagen as gelatin anhydride, hence the  $\begin{array}{c} \text{NH} \\ | \\ \text{CO} \end{array}$  group,

and assumes that this principal valency linkage is split by the action of chromium hydroxide in order to allow of the salt formation. This is, however, neither proven nor probable.

If a further assumption be made that the equivalent weight of collagen is 750 and that 1 collagen equivalent combines with one-third of an atom of chromium, then Wilson (1929) calculates the  $\text{Cr}_2\text{O}_3$  content for monochromium collagenate to be 3.38, which agrees with the figure of 3.4 per cent. put forward by Lamb and Harvey (1916) as the minimum for satisfactorily tanned chrome leather. Wilson describes a chrome leather prepared by him containing double that amount of  $\text{Cr}_2\text{O}_3$  and calls it dichromium collagenate. Thomas and Kelly (1921-4), using special tanning conditions, claim to have prepared tetra- and octo-chromium collagenates. Stiasny suggests that the formation of definite chromium collagenates is extremely doubtful and is not justified from the results of Thomas and Kelly. According to the experimental conditions of concentration, basicity, time and temperature, it would be necessary to assume the existence of very many chromium collagenates if one would conclude from the amount of combined chromium the formation of definite salts. Later in his book, Wilson admits that chrome tanning is much more complicated than the simple neutralisation of the acid collagen by the basic chromium salts. As mentioned above, the question further arises as to how collagen can act as an acid at say pH 3.5 (as in a chrome liquor). This can only be explained by the fact that, though its ionisation at this pH value will be very small there will be a finite number of negatively charged groups scattered throughout this structure, and however small the concentration of negatively charged groups in the collagen structure may be, it is very much larger than would result from the dissociation of the extremely difficultly soluble and hydrolysable chromium collagenate.

(b) *Salt-formation at the Basic Groups of the Collagen.*

Thompson and Atkin (1922) have put forward the theory that chrome tanning is due to salt formation between the basic amino groups of collagen and negatively charged chromium complexes. To justify this they have assumed that negatively charged chromium complexes are present in basic chromium sulphate and chloride liquors. As a support for this idea, they depended upon the presence of such complexes in concentrated boiled chromium salt solutions, the fact that commercial chrome liquors contain such chromium complexes and the work of Pauli (1924), who found negative complexes in aluminium salt solutions. They consider that it would be sufficient for the purpose of their theory if only small amounts of these anionic, acidic chromium complexes were present in ordinary chrome liquors, since on their removal by the basic collagen, they would be immediately and continuously replaced until the action was complete.

But the fact that many anionic chromium complexes do not tan and that chrome liquors containing the whole of the chromium complexes in the kationic state will tan rapidly (F. L. Seymour Jones, 1923) emphasises the point that the theory does not give a completed picture. Many examples could be cited to show that:—

- (1) There are both anionic and kationic chromium complexes which tan.
- (2) There are both anionic and kationic chromium complexes which will not tan.
- (3) Ordinarily, when both kationic and anionic chromium complexes are present, the collagen appears to take up both.
- (4) Chromiates (anionic chromium complexes) can be complete tanning agents under certain conditions (Stiasny, 1924, 1925, 1926; and Gustavson, 1926).
- (5) Chromium complexes which are uncharged exhibit tanning properties in some cases but not in others.
- (6) The nature of the electrical charge on the chromium complex is not the decisive factor in chrome tanning.

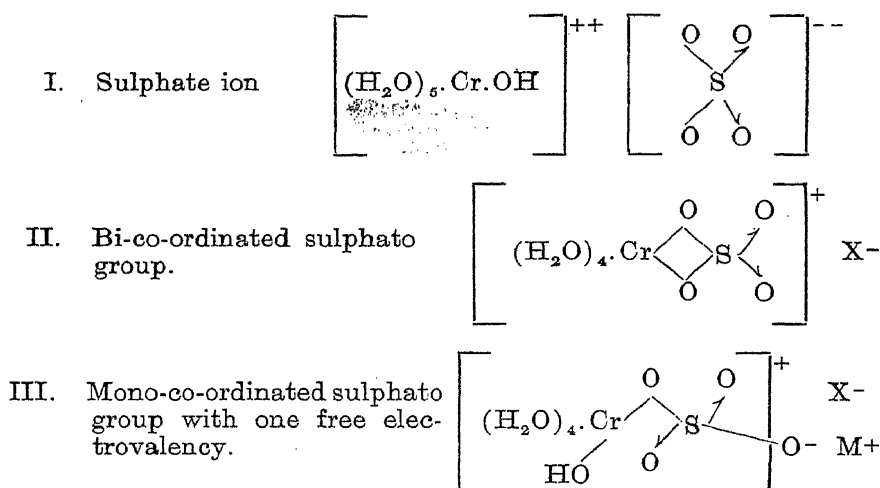
Stiasny is of the opinion that the electro-chemical condition of a chrome salt is not of decisive importance for its tanning action. This viewpoint is commented on by Gustavson (1932), who is of the opinion that salt formation between complex chromium kations and the carboxyl groups of the protein is the essential first stage in chrome tanning. He considers that this salt formation is not the only reaction in the tanning process, but that it must be followed by co-ordination between the chromium complex and the peptide link of the protein, before a true tannage takes place. In view of the stress which he lays on the importance of this second process, his views are considered more fully under co-ordination theories.

Page (1933) is also of the opinion that salt formation between kationic chrome complexes and the carboxyl groups of the collagen is the first stage in chrome tanning, and suggests that the resulting salt formation accounts for the stability of chrome leather towards heat. Though, like Gustavson, he considers that the second stage in chrome tanning is attachment of the chromium

complexes at the peptide link he does not suggest that one complex can be attached at both points on the collagen, but thinks that two separate complexes are involved.

It is convenient at this stage to mention the suggestions which have been made to explain the different effects which are obtained on tanning with chrome liquors which contain differing acid groups. It is well known that chromium chloride liquors do not produce a leather which gives a satisfactory boiling test, while chromium sulphate liquors do. Moreover, the addition of chloride to a sulphate liquor, or of a sulphate to chloride liquor, may interchange the properties of the liquors.

Hudson (1927) first pointed out that the sulphate group may be present in a chromium complex in more than one state of combination. It may exist as a sulphate ion, exerting two electrovalencies, or as a bi-co-ordinated sulphato group, replacing two monovalent groups in the complex, and reducing the positive charge of the complex by two units. It may also replace one co-ordinated group in the complex, reducing the positive charge by one unit, while still exerting one electro-valency and thereby holding a monovalent kation in combination. These states of combination may be symbolised as follows (the linkages between the atoms in the sulphate radicles are shown in full).



These views were also expressed by Stiasny and Balanyi (1928) and later reformulated by Gustavson (1931), who gave somewhat more precise views as to the structure of the different types of compounds. It is evident that the monovalent chloride ion cannot take part in the formation of a compound such as III, and it appears that Hudson and Gustavson consider that by the attachment of groups such as III to the collagen, leather tanned in chrome sulphate solutions obtains its increased stability to boiling water.

### (iii) COMPLEX-CO-ORDINATION THEORIES OF CHROME TANNING.

A further suggested type of linkage between chrome tanning salt and protein involves the assumption that certain groups in

the collagen molecule displace other co-ordinated groups in the chromium complex, forming a chromium compound in which certain groups of the protein molecule are located inside the complex.

Freudenberg (1921) drew attention to the pronounced tendency for the chromium atom to saturate itself co-ordinately with nitrogen compounds and also oxygen compounds and suggested this tendency as being the cause of the combination of chromium and collagen. Such groups as  $\text{NH}_2$ ,  $\text{NH}$  and  $\text{CO}$  would penetrate the chromium complex, displacing other co-ordinative groups, but would still remain part of the collagen molecule, thus furnishing a connecting link. This theory claims to explain the resistance of chrome leather to hydrolysis by water and the ease of de-tanning by tartrate ions with their powerful tendency to displace other co-ordinated groups from the chromium complex. According to Freudenberg the entrance of six negative protein groups into the chromium complex would give the complex three negative charges, permitting its combination with three basic protein groups, thus linking up all the nine valency forces, both primary and secondary. The connecting links involve both the nitrogen and oxygen groups of the protein molecule.\* Stiasny (*Gerbereichemie*, p. 532) in discussing this theory of chrome tanning, pointed out that the experiments of Gustavson, Thomas and Kelly and others are in harmony with the view that tanning with both anionic and kationic chrome salts, and also vegetable tanning, depends upon initial co-ordination between collagen and tan. He considers that the carbonyl oxygen atoms and the nitrogen atoms of the collagen take part in the co-ordination, which may be either directly with the chromium atom or with an atom in one of the co-ordinated groups in the chromium complex. If co-ordination takes place directly with the chromium atom, then a group already in the complex must be displaced, hence a very stable complex may be unable to react in this way, and will exert no tanning action. If the co-ordination is with a group present in the complex the reactive nature of the hydroxo group shown by the formation of  $\text{OI}$  links suggests that it is with this group that such co-ordination will most readily take place. In this case the resulting structure will be analogous to that of  $\text{OI}$  compounds. However, many other methods of co-ordination may be postulated, *e.g.*, those which would involve the hydrogen atoms of hydroxyl groups present either in the chromium complex or in the collagen molecule.

Stiasny's present views on the chrome tanning process (*Le Cuir Technique*, 1933, Dec.)† are, in short, the following.

Two factors are of vital importance for chrome tanning to occur, namely,

- (1) co-ordination between the hydroxyl group in the chromium complex and an active group in the collagen;
- (2) the chromium complex to be of a satisfactory molecular size.

\* An atomic model showing how this can be brought about would be illuminating. (D. J. L.)

† Also communicated in a letter to Dr. Jordan Lloyd, Director of the British Leather Manufacturers' Research Association, from Prof. Dr. E. Stiasny and given above by their kind permission.

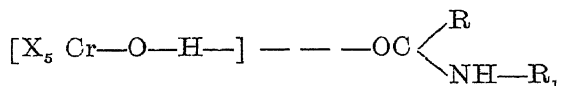
The following points support the idea that it is the *hydrogen* of the hydroxyl group which is linked by co-ordinate valency to the collagen.

(a) Only those chromium complexes which contain the hydroxyl group exert a tanning action.

(b) Basic chromium salts which are completely olated are tanning agents. In these the oxygen of the hydroxyl group is co-ordinately saturated (the co-ordination number of oxygen is 3) and only the hydrogen remains available for co-ordination.

(c) There are many examples (see P. Pfeiffer, *Organic Molecular Compounds*, 2nd Edition), in which it can be shown that the hydrogen of the hydroxyl group can enter into combination with the peptide group of a protein degradation product (*Diketopiperazine*). (See also *Gerbereichemie*, p. 77.)

It is not essential that the co-ordination should occur at a nitrogen atom of the collagen. Many analogous cases support the idea that the linkage takes place at the oxygen of the peptide group (see Pfeiffer l.c. and Freudenberg, 1921). The following example illustrates this idea:—



From this it is evident that the tanning intensity of a chromium complex must depend upon the amount of co-ordinate valency which is available at the hydrogen of the hydroxyl group in the chromium complex. This in turn depends upon whether the hydroxyl group is olated or not and the other groups in the chromium complex. Olated hydroxyl groups exert a stronger tanning effect than unolated, since the oxygen of the olated hydroxyl group is so affected through its co-ordinate linkage (to the second chromium atom) that the amount of valency available for the hydrogen is lessened. The result of this is that the hydrogen of the hydroxyl group can co-ordinate more readily with the collagen. Similarly, each group which decreases the power of co-ordination of the chromium atom (in the complex) exercises a weakening influence upon the tendency to co-ordination of the hydrogen atom of the hydroxyl group. This explains the weakening of the tanning action which is brought about by the entrance of organic acid groups into the chromium complex. It is also obvious that both kationic and anionic chromium complexes will be able to tan so long as the co-ordination power of the hydroxyl hydrogen is sufficient.

In addition, attention must also be given to the questions of molecular size and the capacity to undergo secondary changes. Stiasny does not believe that the active groups in the collagen enter into direct combination with the chromium and enter the chromium complex by displacing other groups such as water molecules, for in this case it would not be easy to see why only chromium complexes containing hydroxyl can tan. He believes, therefore, that the collagen is linked to the hydrogen of the hydroxyl group in the chromium complex.

According to Gustavson (1931), whose views have already been mentioned, in chrome tanning, salt formation first takes place between the complex chromium kation and carboxyl groups of the collagen. This process alone does not form a tannage, co-ordination must next take place between the complex and the peptide link of the collagen. Gustavson apparently considers that hydroxo groups in the complex are active in this co-ordination. The result is the attachment of the complex at two points on the collagen molecule with formation of a ring structure which gives stability to the product. The hydrophilic groups of the collagen molecule are, in the formation of this ring structure, brought into combination with the chromium complex in such a way that they lose their power of co-ordinating with water, that is, they are no longer hydrated. In this way its stability towards water is imparted to the leather. It is generally recognised that the essential part of the tanning process, whether vegetable or chrome, is this inactivation of hydrophilic groups in the collagen by combination with the tan. Gustavson points out that for a satisfactory mineral tannage the central metallic atom of the tan must be capable not only of salt formation, but also of forming stable complexes by co-ordination, and, as he observes, those metals which have incomplete inner electron sheaths (as is found in chromium) form such compounds most readily.

The view that peptide linkages are involved in chrome tanning is strengthened by the work of Thomas and Seymour Jones (1924), who observed that a kationic chrome tannage imparts to hide powder a complete resistance towards tryptic digestion, whereas hide powders tanned with vegetable tans, quinone, formaldehyde and copper sulphate were digested. (The action of trypsin is generally considered to be a hydrolytic scission of peptide linkages.)

#### (iv) SEMI-COLLOID THEORIES OF CHROME TANNING.

Stiasny and co-workers (1923 onwards) laid great stress upon the composition of the chromium complex, especially the size of the complex, as the chief factor in chrome tanning. In the case of a technical tanning process, two conditions have to be fulfilled: (1) the chrome complex must be of a size that it is semi-colloidal, (2) secondary changes must occur which lead to the irreversibility of the chrome tanning process. Tanning power increases with the molecular size of the chromium complex. This molecular size is a function of basicity and the degree of olation. Bjerrum (1907-1910) showed that a molecular weight of 1345 can be attained with chromium chloride solutions made basic with sodium hydroxide. With chromium sulphate liquors made basic with sodium carbonate (which applies to many technical chrome liquors) the molecular weights are still higher, judging by the slow diffusion of this solution through a membrane. Not only for chrome tanning, but also for vegetable tanning it is to be expected that tanning will commence at a suitable molecular size and that the same active groups in compounds of lesser molecular size do not suffice to bring about tanning. The fact that all technically valuable tanning materials (excepting formaldehyde, the tanning action of which requires special consideration) are present in solution in a semi-colloidal form leads to the view that the semi-

colloidal character, that is, a suitable molecular size, is an essential point in the process of tanning. For example, normal chromium sulphate and chromium chloride appear to have simple complexes and give scanty tannages, whereas basic chromium sulphates and chlorides have complexes with more than one chromium atom and are much better tanning agents (see p. 107).

The following table, drawn up by Stiasny, shows these stages in molecular sizes both for chrome tanning and for vegetable tanning.

(1) Chromium complexes containing 1 chromium atom.	Crystallised, no tanning action.
(2) Phenolic non-tans (gallic acid). etc,	
(1) Chromium complexes containing several chromium atoms, partially olated.	} Semi-colloidal, strong tanning action.
(2) Vegetable tannins.	
(1) Chromium complexes containing many chromium atoms, completely olated.	} Colloidal, no or very little tanning action.
(2) Phlobaphenes.	

The second condition for the establishment of an irreversible tannage, to which attention is drawn by Stiasny, is the capacity of a tanning material to undergo secondary changes on the hide fibre. These secondary changes show up in the leather on storage in an increasing resistance towards detanning agents. Chrome leather on storage becomes more resistant to the action of acids, which, perhaps, explains the resistance of chrome leather to deterioration in polluted atmospheres. Vegetable tanned leather on storage becomes more resistant towards water and weak alkalies. The ageing of chrome leather, according to Stiasny, can be satisfactorily explained as being due to the progressive olation of the adsorbed basic chrome salt (combined co-ordinately with the fibre); for olation is facilitated by removal of water (dry storage) and this leads to the formation of complexes which are more resistant to the action of acids. There are, however, secondary processes of a purely physical nature (such as diffusion into the fibre) or a chemical nature (continued valency exchanges with the collagen) or of a colloidal nature (transformation of the tanning colloids from sol form into the gel form) and these must not be lost sight of.

Stiasny claims that this picture of chrome tanning explains why it is that kationic and anionic chrome complexes tan or are not able to tan and why different chrome salts are very different in their tanning action and produce leathers of differing properties since tanning depends upon the constitution of the chromium complex (stability, co-ordination, valency activity) and also upon its molecular size (semi-colloidal character).

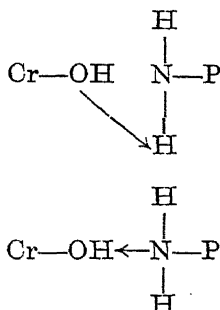
#### (v) DISCUSSION OF THE PRESENT POSITION.

As stated earlier, there appears to be at least one group the presence of which within the chromium complex is essential for the chromium salt to possess tanning properties, namely, the hydroxyl group. It is possible to conceive of a number of different

types of reaction which could occur between the hydroxyl group of the chrome tanning salt and the various active groups in the hide substance, namely:—

(1) The hydroxyl group, since it can react immediately with acids, may react with the acidic groups of the hide substance, leading to the fixation of the hide substance within the chromium complex,  $\text{Cr—OH} + \text{HOOC.P.NH}_2 \rightarrow \text{Cr.OOC.P.NH}_2$ . This would leave the acid fixing function of the protein practically unchanged and would lead to the displacement of water molecules from the OH and COOH groups respectively, both these groups having a tendency to co-ordinate with water molecules.

(2) The hydroxyl group may co-ordinate with the basic groups in the collagen. Co-ordination with the collagen may take place through the oxygen atom or the hydrogen atom of the hydroxyl group, as follows:



This reaction would probably lead to the loss of bound water from both constituents. The OH group and the basic amino group both have a tendency to co-ordinate with water molecules (Jordan Lloyd and Phillips, 1933).

(3) The presence of the hydroxyl groups in the complex is necessary if olation is to occur. By olation particles of large molecular size are built up, and if, as Stiasny suggests (*Gerberei-chemie*, p. 534), such particles are necessary if tannage is to take place, the necessity for the presence of the hydroxyl group is due to the fact that increase in molecular size can take place only when the group is present.

The pronounced tendency for chromium complexes in general to saturate themselves co-ordinately with nitrogen compounds and oxygen compounds opens up another large field for consideration as this tendency might lead to such groups in the collagen as  $\text{NH}_2$ ,  $\text{NH}$  and  $\text{CO}$  penetrating the chromium complex and displacing other co-ordinated groups. These suggestions are discussed above. Attempts have also been made to base a theory of chrome tanning upon the analogy between the action of chromium salts upon permutit and collagen respectively (Appendix B).

Further important points to be borne in mind in a theoretical consideration of the chrome tanning process are the properties of the resulting chrome leather. A very particular property of chrome leather is its resistance to the action of boiling water, that is, its loss of the power to hydrate in water. According to Jordan Lloyd and Phillips (1933), the hydration of proteins in water is

due to the co-ordination of water molecules with the oxygen, nitrogen and hydrogen atoms of the hydroxyl, carboxyl, amino, amido and, to a less extent, the imino and keto groups. They state that the amount of water absorbed by a protein is also dependent on whether the side chains of its molecules bear free amino and carboxyl groups. The reduction of hydration caused by chrome tanning a protein such as hide substance shows that the water combining capacity of the collagen molecules must have been completely abolished and may, therefore, be due to one or both of the following factors:—the groups mentioned above with which the water molecules co-ordinate may have been modified by the chrome tanning process, as suggested earlier, or they may have become co-ordinately linked with basic chromium salts instead of water. If the basic chromium salt so co-ordinately linked reacts easily with acids, thereby losing its hydroxyl group, then since the chromium compound containing no OH groups is no longer a tanning agent, the co-ordinate linkage readily dissolves and the tannage is reversed, that is, dechroming occurs. If, however, the nature of the linkage is in some cases that of an "Ol" linkage, then this does not readily react with acids and the reversal of the chrome tannage is only partial, unless the temperature be raised, corresponding to the amount of such linkage present. This point has already been discussed.

According to Meunier and Viet (1930), "the water absorbing capacity of hide powder is conditional upon the presence of hydrophilic groups in the protein molecule and particularly  $\text{NH}_2$  groups. Combination with these groups brings about a decrease in the water absorbing capacity. In the formation of leather, leaving aside considerations of a physical nature, it has been demonstrated that the chemical phenomena which occur take effect at the free  $\text{NH}_2$  groups in the protein molecule. These are modified and converted into groups less polar towards water. When such a change takes place, true tanning occurs and the product is resistant to prolonged washing in cold water."

A further line of investigation of chrome leather which might be expected to throw some light upon the chrome tanning process is the study of the composition of the chrome tanning salts in the chrome leather. From experiments carried out by the British Leather Manufacturers' Research Association and described in the Second and Third Annual Reports of the Association, it does appear evident that, using oxalic acid, the chrome tanning salt in chrome leathers can be removed from the chrome leather in two stages. The one portion, about 60 - 70 per cent. of the total chromium in the leather, can be removed at room temperatures, about  $20^\circ\text{C}$ ., but the other portion requires a higher temperature (about  $40^\circ\text{C}$ .) for its removal. The second stage in this removal is accompanied by, and is very probably to some extent the result of some destruction of, the leather structure. The chrome tanning salt in chrome leather in its behaviour towards oxalic acid resembles in properties a partially olated basic chromium salt. For instance, the proportion of the chrome tanning salt in chrome leather which is difficultly soluble in oxalic acid can be increased considerably by subjecting the leather to drying and heating (Second Annual Report) and the heating of a basic chrome liquor

increases the percentage of olation. It must also be remembered that heating a basic chrome liquor affects the composition of the chromium complex in that acidic groups which are outside the complex enter the complex.

Chrome leather contains acidic groups and, furthermore, these can occur in at least two types, one in which the acidic group is inside the chromium complex and the other in which it is outside and combined with the protein. Many attempts have been made to evolve a satisfactory method for the determination of these two types of combination, notably by Gustavson (1927), Merrill, Niedercorn and Quark (1928). It would appear that the protein-bound acid is much more readily removed by hydrolysis than chromium-bound acid. Merrill and co-workers found that the ratio of equivalents of chromium-bound  $\text{SO}_4$  to chromium, in the leather examined, was 0.31 to 1. The amount of protein-bound acid is a function of the acidity of the chromium complex. If protein-bound acid is removed by washing or neutralising the leather, then more is set free from the chromium complex. The percentage of protein-bound acid was found to be a linear function of the ratio of the equivalents of chromium-bound acid to chromium when the ratio lay between  $\frac{1}{3}$  and  $\frac{2}{3}$ . When the chromium complex contained less than 1  $\text{SO}_4$  to 6 Cr, no protein-bound acid was formed, but when the chromium complex contained more than 1  $\text{SO}_4$  to 3 Cr, then all acid added to the leather became protein-bound. The percentages of chromium-bound and protein-bound acid are mutually related. It is further to be noted that the distribution of sulphuric acid between the protein and the chromium complex appears to influence the properties of the finished leather.

That the properties of chrome leather are bound up with the presence of acid groups is also generally deduced from the fact that the use of too much alkali in neutralising chrome leather, with the consequent removal of the acid groups, destroys the quality of the leather which, although no chromium is removed, takes on an under-tanned and horny condition. It has been stated, however (Elöd and Siegmund, 1932), that it is possible to remove the whole of the acidic groups from chrome leather by electrodialysis between platinum electrodes and still have a material which is "electrolyte free," will stand the boiling test and which is not horny or tinny, when finished in the usual way.

As a result of chrome tanning, collagen undergoes an alteration of its iso-electric point. Using the dye technique, Gustavson (1926) (see also Wilson, 1929, p. 687, and Stiasny, 1931, *Gerbereichemie*, p. 532) found that the chrome tanning of hide powder with a kationic chrome liquor caused the iso-electric point of the hide powder to rise from  $\text{pH} = 5$  to  $\text{pH} = 6$  to 7, while tanning with anionic chrome liquors (oxalato-chromiate liquors) caused a fall to  $\text{pH} = 3.8$  to 4.8. This was considered to be a strong indication that kationic chromium combines predominately with the acid groups of the protein and anionic chromium with the basic groups of the protein. (Vegetable tanning causes a shift in the iso-electric point of collagen from  $\text{pH} = 5$  to  $\text{pH} = 4$ , indicating that the tannin combines with the basic protein groups.)

In very many of its properties, freshly tanned chrome leather closely resembles chromium salts in general. For example, on standing horsed up in the wet condition, chrome leather undergoes slow hydrolysis with the liberation of acid and the leather becomes acid to litmus. In the neutralising operation the chrome leather is acted upon by the sodium salt of a weak acid, usually boric acid, double decomposition occurs and part of the sulphuric acid in the chrome leather is converted into sodium sulphate. A similar change occurs whenever the sodium salt of a weak acid is added to freshly tanned wet chrome leather. This also occurs in the fatliquoring operation in which the reacting salt is often the sodium salt of a fatty acid, such as stearic or palmitic acid (as in soap).

In addition to withstanding the action of boiling water, chrome leather has the special property of being very difficult to re-wet after it has been dried. It is, however, possible to treat chrome leather in the blue so that it will re-wet easily after being dried out. The leather so treated, however, differs from an undried blue in its reactions to dyes. A satisfactory theory of the dyeing of chrome leather should give the key to this problem. Another feature relating to chrome leather which requires consideration is the small percentage of chromium which is present in ordinary chrome leather. For example, an amount of chromium of 2—2.5 per cent. (as chromium) can be considered a satisfactory tannage, the corresponding amount of hide substance being about 68 per cent. Fifty-two parts by weight of chromium (1 g. atom) would, therefore, be the amount of chromium associated with about 1600 parts of collagen or hide substance, that is, about 280 parts of nitrogen. About 3.8 per cent. of this hide substance is present as  $\text{NH}_2$  groups. That is, about 60 parts or a minimum of  $3\text{NH}_2$  groups per atom of chromium. An atom of chromium in a 33 per cent. basic chrome liquor is associated with one  $\text{SO}_4$  group. Thus the  $\text{NH}_2$  groups in hide substance are more than sufficient in number to react with the sulphuric acid or  $\text{SO}_4$  groups usually present in the chrome liquor in an ordinary one-bath tannage.

Yet another property of chrome leather which has been used to throw light on the chrome tanning process and which has been mentioned earlier is that chrome leather is not acted upon by trypsin (Thomas and Seymour Jones, 1924), that is, there is no doubt that the peptide link must be involved.

To sum up, the principal points which must be borne in mind in any consideration of chrome tanning are as follows:—

- (1) The composition of the tanning bath with special reference to the nature of the groups in the chromium complex, the effect of hydrolytic and olation changes, particle size and so on.
- (2) The nature of the active groups in the hide substance or collagen and their affinities for and possible reactions with the various groups in the chrome tanning salt.
- (3) The changes which occur during the tanning process, such as the initial uptake of chromium salts of low basicity, the alteration in the isoelectric point of the collagen and so on.

- (4) The properties of the chrome leather, such as its resistance to the action of boiling water, the effect of dechroming agents, the chemical analysis of the leather, hydrolytic and ageing changes, the effect of neutralising and fatliquoring, of tanning with other tanning materials, the difficulty of wetting back dried out chrome leather, the stability of the leather to the action of trypsin and so on.

From this brief survey, it is not to be expected that the mechanism of chrome tanning will be explained by a simple theory. There are, indeed, many overlapping theories of chrome tanning and several of these account equally well for some of the phenomena met with.

#### SUMMARY.

1. Combination between basic chromium salts and collagen by primary valencies (electrovalencies) may occur as a first stage in the tanning process to some extent.

2. The main chemical reaction in tanning is due to a co-ordination (by secondary valencies) of the chromium complex and the collagen. There is also the possibility of co-ordination between some group (probably the amino group), and the chromium atom of the complex, displacing a group previously present in the complex.

Possibly centres of co-ordination can be postulated between either the O or the H of the hydroxyl groups in the chrome complex, and the  $\text{NH}_2$ ,  $\text{COOH}$  and  $-\text{CONH}-$  groups of the collagen. This linkage is probably similar to olation.

3. Chrome leather resists the action of boiling water. This is attributed to the inactivation of the hydrophilic groups of the collagen.

4. Chrome tanning protects the peptide link from the action of proteolytic enzymes (trypsin).

5. The character of the acido group in the chrome complex influences the character of the leather.

6. Certain acids, notably oxalic acid, can partially reverse the chrome tanning process. The partially dechromed leather loses its resistance to boiling water. Complete removal of the chromium can be effected by oxalic acid at high temperatures but only under conditions which destroy the collagen fibre.

7. Chrome tanning always takes place in acid liquors. The collagen, therefore, carries an excess of positively charged centres.

In the more commonly used chrome tanning liquors, the chromium complexes are also positively charged. Negatively charged and neutral complexes can also tan.

8. All chromium compounds which act as tans have hydroxyl groups in the complex.

9. Tanning properties appear only to be found between certain limits of size of chromium particles (semi-colloidal). Smaller particles do not tan satisfactorily; larger particles do not tan, perhaps because they do not diffuse into the collagen fibre.

Increase of molecular size of chromium particles is favoured by the withdrawal of acid through salt formation with the basic groups of the collagen.

10. For tannage to occur, the active centres (electrically charged or hydrated) of the collagen molecules must be depolarised or inactivated by loss of electric charge or elimination of water.

## APPENDIX A.

### THE EFFECT OF VARIOUS PRE-TREATMENTS OF THE COLLAGEN UPON SUBSEQUENT CHROME TANNING AND ITS BEARING ON THEORIES OF CHROME TANNING.

Very many experiments on these lines have been carried out in order to throw light on the mechanism of chrome tanning, such as the deamination of collagen, pre-treatment with vegetable tannins or quinone and so on.

#### (a) *The Effect of Deamination.*

In the chrome tanning of deaminised hide powder (prepared by treatment with nitrous acid, then washed, dehydrated with alcohol and dried), Thomas and Foster (1926) and Gustavson (1926) found that deamination lessened the chromium uptake from solutions containing kationic chromium complexes, which agrees with the findings of the British Leather Manufacturers' Research Association (Second Annual Report, p. 97; Third Annual Report, p. 58). The uptake of chromium from solutions containing anionic chromium complexes is also decreased. If, as Wilson, Thomas and Gustavson assume, the combination of kationic chromium complexes occurs through the carboxyl group of the collagen, then deamination should exert no influence on this process. That both kationic and anionic chromium complexes suffer a reduction in uptake in the same way demonstrates clearly, according to Stiasny, that the nature of the electrical charge on the chromium complex does not possess decisive significance. It is suggested that the reduction in chromium uptake is caused in both cases by the fact that deamination brings about an alteration in the structure of the collagen (hide powder) of such a nature that the active surface is lessened.

The experimental findings are in line with the view of chrome tanning that one of the reactions involves the entry of nitrogen groups into the chromium complex and also with the view that a determining factor in chrome tanning is the ability of the chromium complex to combine with protein groups by co-ordination. Gustavson (1926) suggests that a disturbance of the basic protein groups as in deamination has an influence on the activity of the acid protein groups and *vice versa*. It is not safe to say, unconditionally, that because a change in character of the basic protein groups caused a change in the acidity of chrome tanning it follows that the combination must have been with the basic protein groups. A strong indication that kationic chromium combines predominantly with the acid groups of the protein and that anionic chromium combines with the basic groups is indicated by the facts that the tanning of hide powder with kationic chromium causes a rise in the iso-electric point from pH 5 to pH 6·7, and anionic chromium a fall from pH 5 to pH 3·8 - 4·8.

(b) *The Effect of Pre-tanning with Tannin or Quinone.*

The experiments of Thomas and Kelly (1926), in which the effect of the vegetable tanning of hide powder upon subsequent chrome tanning was investigated, could not be looked upon as providing support for the chrome collagenate theory. A reduction in the chromium uptake (from a 33 per cent. basic sulphate solution) caused by pre-tannage of the hide powder with mimosa could perhaps lead to the conclusion that vegetable tans and kationic chrome complexes are linked to the same groups in the collagen. The opposite charge of these two tanning substances, however, makes this seem improbable if one considers tanning as a linking of principal valencies. In this case, the vegetable tanning can be considered to localise at the  $\text{NH}_2$  groups of the collagen and the kationic chromium complexes at the acid groups ( $\text{COOH}$ ) as is suggested by supporters of the salt formation theory. What has been said above with regard to a pre-tannage of collagen with vegetable tannins applies also to the experiments in which quinone was used for pre-tannage. Thomas and Kelly (1926) found that pre-treatment of hide powder with quinone lessened the subsequent uptake of chromium from a 33 per cent. basic chromium sulphate solution.

(c) *Vegetable Tanning following Chrome Tanning.*

Gustavson (1927) chrome tanned hide powder and followed this up by treatment with vegetable tannin. He found that the pre-tannage with kationic chromium complexes caused an increase in the uptake of vegetable tannin whilst a pre-tannage with anionic chromium complexes had the opposite effect. These findings are contrary to those of numerous other observers who found that the combining capacity for vegetable tannins is lessened by first chrome tanning the hide powder, using the usual kationic chrome liquors. An observation of Wood (1908) bearing on these points is of interest. He found that gelatin jellies after treatment with a basic chromium chloride took up the same amount of vegetable tannin as if no pre-tannage with chromium had occurred. Gustavson explained his findings by assuming that the combination of chromium with the acid groups renders the basic groups more reactive. This is not compatible with the view that kationic chromium and vegetable tannins become attached to the same groups in the protein molecule. There is also the possibility of the tannin becoming attached to the chromium as well as the protein in leather tanned with kationic chromium. Gustavson (1924) showed that tannin can penetrate the chromium complex, becoming co-ordinately bound.

(d) *Simultaneous Tanning with Chromium Salts and Vegetable Tannins.*

This gave a lessened uptake of chromium (Burton, 1923) which Gustavson (see above) attributed to the formation of complex compounds between the chromium salt and the vegetable tannin.

(e) *Pre-treatment with Neutral Salts.*

Gustavson's experiments (1926), in which he studied the effect of the pre-treatment of collagen with neutral salts upon chromium uptake, are of considerable significance. The collagen (hide

powder) was treated with various solutions of neutral salts (mostly molar solutions for 14 days' treatment), then exhaustively washed with water, dehydrated with alcohol, dried and then tanned with solutions of kationic and anionic chrome complexes respectively. The pre-treatment had the purpose of satisfying the active auxiliary valencies between the various groups in the collagen for water and neutral salt. The order of activity of the neutral salts was that of the Hofmeister series. In the subsequent chrome tanning, no differences were evident in the chromium uptake of the various treated hide powders with the kationic chrome liquors, whilst for the anionic chrome liquors, the differences in the chromium uptake were very considerable. With increasing "salt" effects, the chromium uptake increased. The same phenomenon has been observed by Gustavson for vegetable tanning.

Gustavson concluded that anionic chrome complexes act as tanning materials through the co-ordinative power of the chromium. By the pre-treatment with neutral salts those groups in the collagen which take part in co-ordination are affected in their power of co-ordination, and this makes itself effective in an increased chromium uptake. Kationic chromium complexes act through their principal valencies on the carboxyl groups in the collagen and there is, therefore, no effect on the chrome tanning in this case as a result of pre-treatment by neutral salts.

Page and Page (1927) measured the effect of neutral salts on the swelling of hide at various pH values. Some of the changes brought about persisted after removing the salts by washing.

All this shows how extremely complex are the reactions resulting from the addition of neutral salts to a chrome liquor. The salt affects the protein, the chromium complex, and by its hydration all the dissolved substances. For example, the fixation of chromium from a 40 per cent. basic chromium chloride can be appreciably increased by the addition of various soluble chlorides, although only part of the effect can be attributed to the action of the added salt upon the protein.

(f) *The Effect of Pre-treatment with Acid or Alkali, Liming, Enzyme Pre-treatment and Pickling.*

Gustavson (see Wilson's *Chemistry of Leather Manufacture*, p. 690) also studied the effect of the pre-treatment of collagen with acid and alkali and also the effect of liming, enzyme pre-treatment and pickling upon subsequent chrome tanning. The acid or alkali was removed from the pre-treated collagen before it was tanned with various chrome liquors. The pre-treatment had relatively little effect upon a kationic tannage with a 37 per cent. basic chromium sulphate liquor, but a chromiate tannage and a 60 per cent. basic chromium sulphate tannage were very much alike and gave curves (vertical axis =  $\text{Cr}_2\text{O}_3$  fixed) for the uptake of chromium which followed the swelling curve of hide shown as a function of pH value. According to Gustavson, swelling causes a permanent stretching of the hide fibres and leaves it with a specific surface roughly proportional to the degree of swelling it has previously undergone. On the other hand, the secondary valency forces of the protein are liberated in proportion to the swelling. These

influence the combination with vegetable tannin or with anionic chromium but have only a slight effect upon the combination with kationic chromium which takes place by means of primary valency forces.

The duration of liming had a very great effect upon consequent chrome fixation from chromiates, a 50 per cent. basic chromium sulphate liquor and even a 40 per cent. basic chromium sulphate liquor. This last finding seemed to be exceptional, but it is probably bound up in some fundamental change in the collagen. This idea is supported by the fact that unlimed hide takes up less acid from a solution at a pH of 2.07 than does a limed and delimed hide.

Both pepsin and trypsin were tried at pH values of 2.2 and 8.0 respectively. The results suggested to Gustavson that the enzymes may remove the activated protein groups and lessen the fixation of chromium. Wilson believes that the so-called activation by electrolytes is a step in the conversion of collagen to gelatin and that enzymes hydrolyse the gelatin, leaving the less reactive collagen behind.

In the experiments on the effect of pickling, Gustavson found that there appeared to be optimum values, judged by the fixation of chromium, for acid and salt concentration, time of pickling and temperature, depending upon the conditions obtaining in the tanning bath to follow.

## APPENDIX B.

### THE ACTION OF CHROME LIQUORS UPON PERMUTIT AND ITS BEARING ON THEORIES OF CHROME TANNING.

Gustavson (1924) found that permutit (a double silicate of aluminium and sodium) would take up from a chromium sulphate solution an amount of chromium which increased with increasing basicity of the chromium salt solution. He explained this from the standpoint that with increasing basicity the electrical charge per 1 atom of chromium decreases. If the permutit "tanning" is regarded as an exchange reaction between the sodium in the permutit and the chromium in the chrome liquor, then one atom of sodium would be displaced by one chromium complex with one unit of charge, as in a 66.7 per cent. basic solution; two atoms of sodium by one chromium complex with two units of charge, as in a 33 per cent. basic solution; and three atoms of sodium by one chromium complex with three units of charge, as in a normal chromium sulphate solution. This reaction was found to hold for normal chromium sulphate solutions but not for chromium chloride liquors as the 33 per cent. basic liquor  $[(\text{H}_2\text{O})_5\text{Cr.OH}]\text{Cl}_2$ , gave an interchange of three sodium atoms for one chromium complex instead of two sodium atoms. Wilson (*Chemistry of Leather Manufacture*, p. 674) explained this by assuming that the basic chromium complex in its combination with the permutit loses its basic group (OH), this being displaced by water. The explanation is not a happy one, for hydroxyl groups are strongly held in the chromium complex and it is extremely unlikely that basic OH groups would be displaced from the complex (Stiasny, *Gerbereichemie*, p. 528). Wilson further

considers that Gustavson's work on permutit confirmed the chromium collagenate type of theory of chrome tanning, but with considerable modification, as instead of dealing with a simple tri-valent chromium kation, one is dealing, in chrome tanning liquors, with complicated chromium complexes of variable size, composition and electrical charge.

Later experiments by Kinzer (1930) have shown that in the action of chromium salt solutions upon permutit, the permutit is attacked by the free acid formed from the chromium salt solutions by hydrolysis so that particularly with normal chromium salt solutions much larger amounts of sodium are brought into solution than correspond with the amount of chromium taken up. In many cases the solutions were found to contain aluminium derived from the permutit. It therefore appears unwise to draw too close a parallel between experiments with permutit and chrome tanning.

However, the following points of resemblance exist between the action of chrome liquors upon permutit and upon collagen:—

- (1) Larger amounts of chromium are removed from chromium sulphate liquors than from chromium chloride liquors of the same basicity and chromium content.
- (2) The amount of chromium taken up increases with increasing basicity of the chrome liquor.
- (3) The amount of chromium taken up is increased as a result of olation.
- (4) Anionic chromium complexes containing sulphate groups are taken up freely and irreversibly to washing with water.

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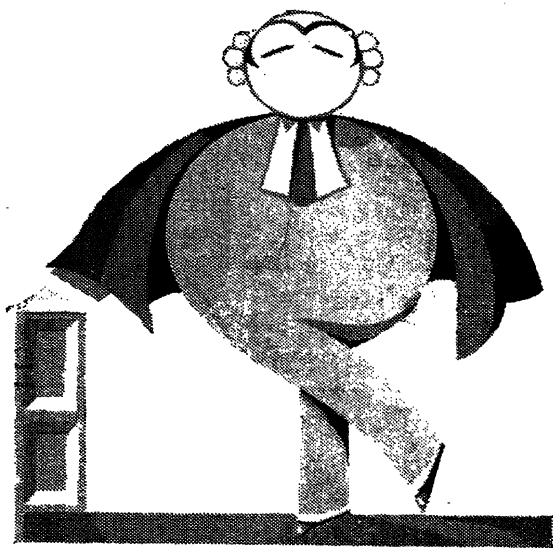
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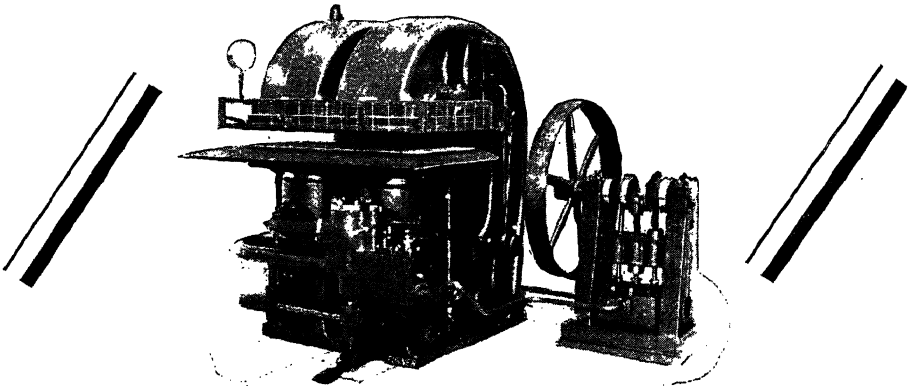
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